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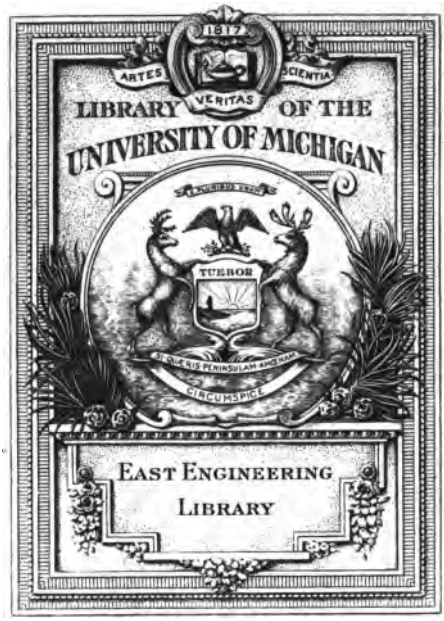
# The Manufacture of Metallic Articles Electrolytically—Electro-Engraving

PFANHAUSER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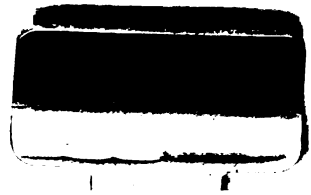

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# Manufacture of Metallic Articles Electrolytically. — Electro-Engraving

BY

DR. W. PFANHAUSER

Manufacturer of Machinery, Apparatus and Chemical Preparations for Electroplating and Galvanoplastics

---

Authorized English Translation

BY

JOSEPH W. RICHARDS, M.A., A.C., Ph.D.

Professor of Metallurgy, Lehigh University; Past President of the American Electrochemical Society

EASTON, PA.
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1906

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# MONOGRAPHS

—ON—

# APPLIED ELECTROCHEMISTRY

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And other experts.

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# CONTENTS


| | PAGE |
|---|---|
| I. HISTORICAL REVIEW | 1 |
| A. Introduction | 1 |
| B. Advances in the Art | 1 |
| II. BATHS FOR COPPER GALVANOPLASTY | 3 |
| A. Neutral Bath | 3 |
| B. Work of Chassy | 3 |
| C. Foerster's Work on Quantitive Precipitation of Copper | 4 |
| D. Studies by Hübl, 1886 | 6 |
| III. PHYSICAL PROPERTIES OF THE COPPER DEPOSIT | 14 |
| A. Hübl's Investigations | 15 |
| IV. BEHAVIOR OF COPPER ANODES | 25 |
| V. CONSTANTS OF THE BATH AND CALCULATION OF THE AMOUNT OF DEPOSIT | 28 |
| VI. INDUSTRIAL PLANTS | 32 |
| VII. PARTICULAR DEVICES FOR SPECIAL PURPOSES. PRODUCTION OF UNIFORM DEPOSITS | 37 |
| A. Process of Bauer | 39 |
| B. Process of Anderson | 39 |
| C. Wurttemberg Process | 40 |
| D. Dumoulin Process | 42 |
| E. Method of the French Copper Company | 43 |
| F. Devices for Loosening of the Precipitates | 43 |
| G. Process of Sutherland | 43 |
| H. Process of Reinfeld | 44 |
| I. Method of Holl | 44 |
| J. Elmore's Process | 45 |
| K. Nussbaum's Process | 46 |
| L. Collapsible Forms | 46 |
| M. Elmore's Process | 47 |
| N. Collapsible Moulds of Gerhardi & Co. | 49 |
| VIII. MANUFACTURE OF METALLIC POWDERS AND THE LIKE | 52 |
| A. Process of the Societe Civile | 54 |
| B. Process of Hoepner | 55 |
| C. Process of Hüber & Sachs | 60 |
| IX. MANUFACTURE OF METALLIC FOIL | 61 |
| A. Process of Reinfeld | 61 |
| B. Process of Endruweit | 61 |
| C. Elmore's Process | 63 |

D. Desolle's Process ..... 63
E. Process of Cowper-Coles ..... 64
F. Process of Landauer & Co. ..... 64
G. Process of Brandt & Nawrocki ..... 69
H. Process of Endruweit ..... 70
I. Process of Schroeder ..... 70
J. Sheet Gold by Swan's Process ..... 72
K. Production of Plane Surfaces, Rieder's Process ..... 72
L. Elmore's Process ..... 75
X. Production of Wire, &c. ..... 76
A. Process of Elkington ..... 76
B. Fox's Process ..... 76
C. Acheson's Process ..... 76
D. Tavernier's Process ..... 77
E. Process of Swan ..... 78
F. Process of Sanders ..... 84
G. Process of Forsythe and Fletcher ..... 91
H. Process of Cowper-Coles ..... 91
XI. Manufacture of Bodies of Large Size ..... 93
A. Process of J. Klein ..... 93
B. Nussbaum's Process ..... 100
C. Sutherland's Process ..... 105
D. Elmore's Process ..... 105
E. Process of Davis & Evans ..... 106
F. Process of A. Krueger ..... 106
XII. Manufacture of Parabolic Mirrors ..... 108
A. Process of the Elmore German and Austro-Hungarian Metal Company, Limited, and P. E. Preschlin ..... 108
B. Process of Cowper-Coles ..... 108
XIII. Manufacture of Tubes ..... 117
A. Process of the French Copper Society ..... 123
B. Process of Dumoulin ..... 125
XIV. Electrolytic Etching ..... 130
A. Burdette's Process ..... 131
B. Hall & Thornton Process ..... 133
XV. Electrolytic Engraving ..... 138
A. Introduction ..... 138
B. Engraving with Partial Covering ..... 139
C. Electro-Engraving Processes ..... 140
D. Rieder's First Investigations ..... 141
Appendix ..... 149

## PREFACE

While giving in the present small treatise a compilation of the published information in the field of the manufacture of metallic articles by electrolytic methods, I must say that it is impossible to treat such an extensive field in so small a space in such a manner that the technician, seeking for minute details, would not be compelled to seek further information in special publications.

The material can only be handled in the form of abstracts, but in many cases the incompleteness of the work is entirely due to the fact that it has been impossible to publish all the secrets of the trade. On these grounds I must unfortunately restrain myself in many cases from presenting such important data as to the profitableness of most of the processes; yet in many cases I have attempted to supply the lack of such data by my own calculations, where the firms using the processes were unwilling to furnish such data. In many cases profitableness of the processes may be deduced from the data concerning the process, which have been given.

Many of the processes meet with a great many unforseen difficulties, such as in the details of apparatus or of technical practicability; many on the contrary cost more than the old processes.

The thoughtful artisan, however, will find much food for reflection in many of the processes described, and be induced to experiment further in one or another direction, or to attempt to perfect some of these processes, and I will consider my task sufficiently completed if I have furnished the impulse to this work by my modest efforts.

VIENNA. W. PFANHAUSER.

# I. HISTORICAL REVIEW.

## INTRODUCTION.

M. H. Jakobi is generally acknowledged as the founder of galvanoplastic reproduction and the industrial development of copper precipitation resulting therefrom. He first presented the results of his pioneer work to the St. Petersburg Academy of Sciences in 1838. However, Jordan and Spencer contested the priority, but it has been proven that these brought their experiments to a practical stage later than Jakobi. Jakobi also, like all workers in galvanoplasty up until the last thirty years, worked with the well-known cell apparatus, which in principle was practically a short-circuited Daniell cell.

In the year 1840 Murray introduced the graphitizing of non-conducting surfaces and in 1842 reproduced the first engraved copper plates by galvanoplastic methods.

## ADVANCES IN THE ART.

The manufacture of useful articles in the electrolytic way could naturally only become practicable with the advent of the modern dynamo machine which thus makes available large quantities of electrical energy. With the increased interest in all such processes which used electricity there was a great increase along experimental lines, towards the bringing of electricity to the service of the metal worker, and thus the circle of application rapidly widened.

As in almost all branches of electrochemistry, so here, detailed information of processes, such as is used by technicians for their exact reproduction, are seldom to be had, and I must, in many cases, limit myself to assumptions, especially where calculations are involved.

At the present time there are a large number of more or less technically available processes, widely divergent electrolytically, for the manufacture of useful articles, in which in general copper is used as the depositing metal; and it is only very recently that

nickel has become of importance, unfortunately only to a limited extent, because in the case of nickel quite serious difficulties are encountered which limit the availability of this otherwise so suitable metal.

It can be said of some of the processes already developed that they are competing successively with the older mechanical ones and many of them will drive out the older processes as soon as the small difficulties which stand in the way of their technical application have been overcome by the general advance of the art.

Nevertheless, electrolysis has open before it a large and profitable field in galvano-technics, when cheap power and raw materials are brought into combination with well organized processes run on a large scale.

# II. BATHS FOR COPPER GALVANOPLASTY.

The most important galvanic bath technically is the copper bath. As the oldest and therefore the best known bath it has been the most thoroughly investigated, and for this reason copper has played the main role in the manufacture of articles electrolytically.

## NEUTRAL BATH.

It has been found that when electrolyzing a neutral solution of copper sulphate, $CuSO_4$, (obtained by boiling it with copper carbonate, $CuCO_3$, and subsequent filtration) there always results brittle copper, which, in being lifted off the cathode, falls in pieces. After continued use of the bath, particularly when employing high current densities, the character of the precipitate improves so that finally perfectly flexible homogeneous metal is obtained. The explanation of the above described facts appears to be found in the assumption that in the neutral solution there is a small quantity of basic sulphate together with the normal salt, which then furnishes traces of cuprous oxide during the electrolysis; or that the latter is formed by reaction upon the already precipitated copper. According to this explanation the brittleness of the deposited copper is explained by its content of cuprous oxide.

## WORK OF CHASSY, 1894.

Chassy[1] furnishes some interesting contributions on this subject. This investigator found out that using a cathode current density of 1 ampere per square decimeter and electrolyzing a saturated copper sulphate solution at 100° C., there was obtained a red precipitate tarnishing a peculiar blue, and consisting of small red cubic and octahedral crystals of cuprous oxide, $Cu_2O$. At temperatures below 100° C. much copper appears in place of cuprous oxide; at 40° C. and thereunder only the metal is precipitated. Similar results were obtained by Chassy by decreasing the concentration or the current density.

[1] Comptes rendus, 1894, 119, Vols. 4-5. 271.

## FOERSTER'S WORK ON QUANTITATIVE PRECIPITATION OF COPPER.

Very soon after this Dr. F. Foerster published his interesting communication upon the phenomena of the electrolysis of copper sulphate solutions, which he brought out in connection with his studies upon the copper voltameter. Foerster set forth the following fundamental laws:[1]

1. With current densities under 0.01 ampere per square decimeter the action of the current upon the concentrated copper sulphate solution at the ordinary temperature consists in a liberation of cuprous ions at the cathode. With increasing current densities more and more cupric ions are completely discharged and relatively fewer cuprous ions produced by the current, without, however, the production of the latter completely ceasing even at high current densities.

2. The tendency of the cupric ions of the sulphate solution to pass over into cuprous ions increases very markedly with the temperature so that at 100° C. the current produces almost exclusively cuprous ions at the cathode, even with current densities of 0.03 ampere per square decimeter in a concentrated copper sulphate solution.

3. The production of cuprous ions can take place in copper sulphate solutions without the influence of the current, as in cupric chloride solutions, by the action of metallic copper upon the cupric ions of the cupric sulphate solution:

$$Cu + \overset{++}{Cu} = 2\overset{+}{Cu}_2.$$

This action proceeds until the cupric sulphate solution is saturated with cuprous sulphate. It is difficult to determine in the case of copper sulphate solutions to what extent the formation of cuprous sulphate depends upon this solution of copper or upon pure electrolytic action; Foerster thinks the latter to be the simplest and most probable factor.

4. Under similar conditions more cuprous ions will be formed

[1] Zeitschr. f. Elektrochemie 3, 480 and 481.

[2] This fact was established a long time ago by Jakobi (see Wiedemann, Zeitschr. f. Elektrochemie 2, 510) but the knowledge of it apparently had no influence upon the later developments of the subject.

in a sulphuric acid solution, the greater the concentration of the cupric ions present.

5. If the solution is neutral the cuprous sulphate produced suffers hydrolysis as soon as its concentration has exceeded a certain limiting value. The equation of the change is

$$2\overset{+}{Cu} + \overset{--}{SO_4} + H_2O = Cu_2O + 2\overset{+}{H} + \overset{--}{SO_4}.$$

By reason of this reaction cuprous oxide is often separated upon the cathode in crystals having an adamantine lustre, leaving in solution free sulphuric acid.

6. If the solution is sufficiently acid no hydrolysis will take place and much larger quantities of cuprous ions will remain in solution than if the latter is neutral.

Even in this case, however, there is a limit to the enrichment of the solution in cuprous salt, for as soon as the relative concentration of the cuprous ions to the cupric ions has passed a certain limit the former change back to cupric ions thereby separating out metallic copper:

$$2\overset{+}{Cu} = \overset{++}{Cu} + Cu.$$

Referring back to the phenomenon of solution described in paragraph 3, we see that we have a reversible reaction

$$Cu + \overset{++}{Cu} \rightleftarrows 2\overset{+}{Cu}.$$

7. There results at the cathode metallic copper by the above described operations from very acid cupric sulphate solutions, also when the current density only produces cuprous ions.

In the latter case the copper might be regarded as separated out "secondarily" and does not form uniform deposits like the copper separated out in the ordinary way from acid solutions, but appears in small single, distributed crystals.

8. If the cuprous ions get to the anode they again take up positive charges and are converted into cupric ions; the current is then doing at the anode, in a measure as this reaction takes place, other work than ionizing the anode itself.

As is seen from the preceding paragraphs the current density used plays an extraordinarily important part even in the correct solution, no less than the content of acid and the temperature of

the solution. The avoidance of the formation of cuprous ions is a fundamental condition for quantitative precipitation of copper and likewise for the obtaining of coherent metal.

Foerster found the results collected together in the following table when electrolyzing acid and neutral cupric sulphate solutions of various concentrations with various current densities.

| $CuSO_4$. | $H_2SO_4$. | Amp per. sq. dm. | Properties of the Cathode copper. |
|---|---|---|---|
| 2.0 | – | 13.0 | At places powdery |
| 2.0 | – | 10.0 | Dense, bright red |
| 1.0 | 1 | 7.0 | Powdery |
| 1.0 | 1 | 4.0 | Strongly adherent, bright red |
| 0.25 | – | 1.0 | Dark red, powdery |
| 0.25 | – | 0.7 | Beautiful, bright red |
| 0.25 | 1 | 1.8 | Dark red, powdery |
| 0.5 | – | 0.3 | Ditto |
| 0.5 | – | 0.15 | Bright red adherent |

In this table the numbers under the headings $CuSO_4$ and $H_2SO_4$ denote the number of gram-equivalents of these materials present in one litre of the electrolyte (by weight the gram-equivalents are 80 and 49 respectively).

Foerster worked wtih stationary electrolytes and the above values are valid only for such.

As early as 1857 Magnus[1] published a work upon "Limiting Values of the Current Density in Copper Sulphate Solutions," and here we may also refer to the work of Karl Ullmann, who reported upon the influence of time upon the phenomena at the cathode in the electrolysis of copper sulphate solutions. It would lead us too far to reproduce at length Ullmann's results, and I content myself with referring to his very interesting original manuscript.[2]

## STUDIES BY HÜBL, 1886.

Arthur von Hübl described in 1886 in the "Mitteilungen des k. u. k. militär- geographischen Institutes," 6, 51 to 96, his fundamental studies upon the properties of electrolytically precipitated copper, and I extract freely from this communication because the physical properties of cathode copper are treated with particular completeness and thus must be of special interest to us. Hübl writes:

[1] Pogg. Ann. 102, (1857) 1 to 54.
[2] Zeitschr. f. Elektrochemie, 3, 516 et seq.

"If an addition of sulphuric acid is made to the copper sulphate solution then both copper sulphate and sulphuric acid take part in carrying the current and both will be decomposed in quantity corresponding to their conductivities.[1] Since the sulphuric acid is very strongly dissociated in comparison to the copper sulphate and therefore is an excellent conductor, the addition of only a few per cent. of acid results in the conducting of the current being done practically by the acid itself. The separating out of copper at the cathode proceeds as follows: that $\overset{+}{H}$ precipitates copper secondarily because of its higher discharge potential, while copper is precipitated primarily only in quantity corresponding to the dissociated fraction of copper sulphate present.

"If the hydrogen finds at its point of evolution an insufficient quantity of copper in the solution, that is if the solution is too dilute in comparison with the quantity of hydrogen produced, then the latter separates out as free gas and results in a loosely coherent deposit of copper. This phenomenon is therefore to be observed; the lower the current density the more dilute the solution in copper sulphate and the greater the addition of sulphuric acid. The beginning of the separation of hydrogen is characterized very plainly by the development of a strong polarization by which the apparent resistance of the electrolyte suffers a sudden increase.

*The Separation of Copper in Granular Form.*

"If the quantity of hydrogen separating out is small in proportion to that of the copper no evolution of gas takes place at the cathode: the hydrogen apparently combines with the copper, forming a hydride, which combined with the pure metal forms a non-homegeneous, powdery, spongy or sandy precipitate of more or less dark color. Only on further increase of the current density, does the quantity of hydrogen set free become so great that it appears in the form of gas bubbles.

*Changes in Concentration During Electrolysis.*

"If the concentration of the bath is investigated during the electrolysis at different places it is found to vary and it may be easily

[1] This explanation is no longer considered valid.—Translator.

proven that a dilution takes place at the negative pole, and at the positive pole a concentration of the solution. In the presence of free sulphuric acid the dilute solution at the cathode will be richer in acid than the concentrated solution at the anode. Hittorf explains these changes in concentration, by the assumption that the ions move with different velocities towards the electrodes (Wiedemann, Elektrizität **2**, 548, 942), while the increase of acid at the cathode is produced by the indirect precipitation of copper by hydrogen.

"The concentrated solution is specifically heavier, the dilute solution lighter than the original, and therefore when the electrodes hang vertical a current of electrolyte rises upwards around the cathode and flows downwards around the anode. The consequence of this phenomenon is that after some time a layer of very concentrated solution is found at the bottom of the vessel while at the surface a very dilute solution and finally only an acid solution is to be found.

"These facts entail many disadvantages in practice and have to be very carefully watched when working with vertical electrodes and are the more in evidence the greater the current density and the extent of the depositing surfaces.

*Inequalities in the Copper Precipitate.*

"The current of solution rising at the cathode is divided quickly into single vertical rising parts by the small irregularities found upon the cathode surface, and since these divided currents vary in their concentration they produce an unequal distribution of the current passing to the cathode. There will be therefore formed vertical lines upon the cathode with gutter-like grooves in between; the lines grow rapidly and therefore increase the difficulty both in consequence of increasing the differences in concentration, as also because the projecting lines receive more copper deposit than the grooves between them.

"A further consequence of these currents is that the copper crystals of which every galvanic deposit consists arrange themselves in certain directions and thereby make the cohesive strength of the precipitate different in different directions.

"The layers of liquid produced in time cause the heavy solu-

tions at the bottom of the vessel bathing the lower end of the anode to cover it with copper sulphate crystals, which, being poor conductors of electricity, introduce resistance. On the other hand the different conductivity of the concentrated and dilute solutions produce an unequal division of the current, so that finally the dilute or simple acid solution on the surface may produce a deposit of non-homogeneous copper. For this reason it will always be observed that the lowest lying part of the cathode grows faster than those parts which are nearer the surface and that the first indication of the production of hydrogen, namely the precipitation of sandy copper, occurs first in the upper part of the electrolyte.

"In order to get a better picture of the stratification of the solution, tests were taken at different depths through a bath containing 19 per cent. of copper sulphate and 3½ per cent. of sulphuric acid, during the course of the electrolysis. The size of the electrodes was about 50 centimeters square, the distance apart, 8 centimeters, and the current strength 40 amperes. After running 7 hours three tests taken from between the electrodes showed the following composition:

1. Test from the surface: 12.7 per cent. copper sulphate, 3.9 per cent. sulphuric acid.

2. Test 25 centimeters under the surface: 21 per cent. copper sulphate, 3.4 per cent. sulphuric acid.

3. Test 50 centimeters under the surface: 29.2 per cent. copper sulphate, 3 per cent. sulphuric acid.

*Concentration Currents.*

"A further evil of the stratification of the liquid is observed if, after shutting off the current, the electrodes are allowed to stand in the bath by themselves for several hours. The copper dipping into the two solutions of different concentration causes concentration currents which pass from the metal in the dilute acid solution above, through the liquid to the concentrated solution below and to the end of the electrode in contact with it, and produce solution of the upper part of the electrode and deposition upon the lower part.

"The existence of currents of this kind was first observed by Buchholz (Gehlens, Journal de Chemie 5, 1808). The upper part

of the cathode of precipitated copper being in dilute acid solution, behaves after the interruption of the current exactly like an anode; its surface is dissolved by $\overline{SO_4}$. As will be later explained at length, there forms, however, on the surface of each anode a loosely coherent dark colored deposit which, when electrolysis is resumed after an interruption, prevents the newly precipitated metal from uniting perfectly with that earlier precipitated. In consequence of this phenomenon which repeats itself at each interruption of the current, the copper precipitated may consist of several loosely coherent layers.

"All the difficulties which are met with in practice in consequence of the inequalities in the solution may be overcome in two simple ways: through a mechanical arrangement for a continual mixing of the bath or by arranging the electrodes horizontally.

*Maximum Current Density.*

"As has already been mentioned, there is formed during electrolysis, if a certain current density is exceeded, a non-coherent precipitate caused by the free development of hydrogen. This is very evidently perfectly useless for practical purposes. But since it is on the other hand very desirable to hasten the galvanoplastic processes as much as possible it is necessary to make use of higher current densities. It is therefore of the greatest value to know this maximum current density which may be used in those baths of different composition, and still produce with certainty faultless, strong and flexible precipitates.

"The results of experiments in this direction are contained in the following table which gives the current densities at which free hydrogen is evolved, immediately upon the closing of the circuit. This is evidenced both by the occurrence of the already described polarization as well as by the occurrence of non-homogeneous dark metallic deposits.

| Concentration of the solution in $CuSO_4$ Per cent. | Current density at which the evolution of hydrogen begins, in amperes per square decimetre. | | | |
|---|---|---|---|---|
| | Normal. | 0.6 % $H_2SO_4$. | 3.0 % $H_2SO_4$. | 6.0 % $H_2SO_4$. |
| 1.0 | 0.32 | .... | .... | .... |
| 2.5 | 1.20 | 0 80 | 0.68 | .... |
| 5.0 | 2.60 | 1.60 | 1.44 | 1.40 |
| 10.0 | 5.12 | .... | 3.40 | 3.20 |
| 15.0 | 7.80 | .... | 5.72 | 4.60 |
| 20.0 | 10.20 | .... | 7.08 | 6.00 |

"From this table it is to be concluded that:

1. The allowable current densities are approximately proportional to the concentration of the solution.

2. A very small addition of sulphuric acid lowers very much the allowable current density, while a further addition of acid exercises a relatively small influence. This fact is explained very simply by the relatively higher conductivity of the sulphuric acid. If to a 20 per cent. solution of copper sulphate, 1 per cent. of sulphuric acid is added it will share to an equal extent in the conduction of the current; while with 5 per cent. of sulphuric acid the acid does practically all the current conducting. It the last case almost all the copper precipitated is separated out secondarily: therefore, a still further addition of sulphuric acid must be almost without influence.

"In practical galvanoplasty a number of conditions arise, however, which influence very unfavorably the current densities which can be used in practice.

"To start with, it must be observed that the solution at the negative electrode and at the surface of the bath becomes poorer in copper; and that, therefore, the development of free hydrogen may occur often when using current densities below the normal maximum value, if the copper content of the layer of liquid becomes so decreased by electrolysis that it no longer suffices to furnish copper in exchange for hydrogen. In consequence of this condition it is scarcely possible in practice to use more than one-half, usually only one-third, of the above given values of current densities. If, however, active circulation of the fluid is provided for, so that the negative electrode is continually supplied with new copper sulphate solution, faultless precipitates will be obtained up to the maximum values given. With very energetic agitation of the solution even these numbers can be greatly exceeded, since investigations on a small scale have shown that with these conditions a one per cent. neutral bath may be worked with 0.8 ampere, a 20 per cent. solution with 18 amperes current density and still give practically useful deposits. From practical considerations, however, only a very gentle agitation of the bath is possible, in which case the use of one-half to two-thirds of the maximum density named appears to be all that is allowable.

"From these remarks it appears that the highest current density practicable in galvanoplastic practice is between the following limits.

| Composition of the bath. | Maximum current density practicably allowable for solutions in amperes per square decimeter. | |
|---|---|---|
| | At rest. amperes. | In gentle motion. amperes. |
| 15% copper sulphate, neutral | 2.6–3.9 | 3.9–5.2 |
| 15% copper sulphate + 6% sulphuric acid | 1.5–2.3 | 2.3–3.0 |
| 20% copper sulphate, neutral | 3.4–5.1 | 5.1–6.8 |
| 20% copper sulphate + 6% sulphuric acid | 2.0–3.0 | 3.0–4.0 |

"The current density could be still further increased if it were possible to use a more concentrated copper solution, which, however, is not practicable when using copper sulphate because on the one hand the solubility of this salt is very noticeably diminished by the addition of the necessary sulphuric acid, and because on the other hand the concentration of the liquid layer around the anode increases during the electrolysis and yet must always possess the capability of dissolving the newly formed sulphate.

*Solubility of Copper Sulphate.*

"The solubility of copper sulphate in dilute sulphuric acid of different concentrations has been determined experimentally at 55° C. and gave the following results:

In the presence of 0% $H_2SO_4$ 1 liter of saturated solution contains 39 gms. $CuSo_4$.

In the presence of 1% $H_2SO_4$ 1 liter of saturated solution contains 348 gms. $CuSO_4$.

In the presence of 2% $H_2SO_4$ 1 liter of saturated solution contains 308 gms $CuSO_4$.

In the presence of 3% $H_2SO_4$ 1 liter of saturated solution contains 280 gms. $CuSO_4$.

In the presence of 4% $H_2SO_4$ 1 liter of saturated solution contains 260 gms. $CuSO_4$.

In the presence of 5% $H_2SO_4$ 1 liter of saturated solution contains 253 gms. $CuSO_4$.

In the presence of 6% $H_2SO_4$ 1 liter of saturated solution contains 245 gms. $CuSO_4$.

In the presence of 8% $H_2SO_4$ 1 liter of saturated solution contains 231 gms. $CuSO_4$.

In the presence of 10% $H_2SO_4$ 1 liter of saturated solution contains 215 gms. $CuSO_4$.

In the presence of 12% $H_2SO_4$ 1 liter of saturated solution contains 197 gms. $CuSO_4$.

In the presence of 14% $H_2SO_4$ 1 liter of saturated solution contains 180 gms. $CuSO_4$.

"It is to be seen from these figures that in the presence of 4 per cent. of sulphuric acid not more than 26 per cent. of copper sulphate can be dissolved, and therefore a solution of this concentration can no longer be used. For a gently agitated bath a solution containing, at the highest, 20 per cent. may be used; but in a bath not stirred separation of crystals on the anode will begin even at this concentration if the highest curent densities are used and 4 per cent. of sulphuric acid is present. It is finally self-evident that the temperature of the bath may also exert an important influence upon the above described conditions and under some circumstances may also be the determining factor of the allowable current density.

# III. PHYSICAL PROPERTIES OF THE COPPER DEPOSIT.

The endeavor of galvanoplastics must be to produce a copper deposit with properties suitable for the purpose desired,—that is, with certain definite physical properties. Since these properties must be within certain limits, it is necessary to know those factors which determine the qualities of the deposits obtained.

### INFLUENCE OF FOREIGN ADMIXTURES.

The views on this subject are contradictory. This is explained by the great difficulties which are experienced in carrying out such investigations. The properties of the deposit are without doubt often very largely influenced by secondary processes connected with changes or small impurities in the bath, and it is often impossible to recognize and trace out to their limit the phenomena in question. If we take into consideration the changes which copper, like other metals, undergoes through the presence of traces of foreign bodies, for instance even by cuprous or cupric oxide, there can be no doubt that similar considerations must be of an important influence upon the properties of the galvanic deposit. There is no doubt of this in the case of deposits gotten from the acetate or from cupric chloride, as also from basic copper solutions.

### STRUCTURE.

Aside from the secondary processes taking place and the influence of impurities in the bath, the physical properties of the copper are considerably influenced by the structure of the same. The structure is crystalline but the single crystals are more or less developeed. This consideration as well as their orientation must determine largely the strength, elasticity and hardness, etc., of the metal.

Since the metal is separated from a copper solution by the electric current, the structure of the crystalline aggregate must be determined by two factors; composition of the bath, and current strength.

Two views have been advanced respecting the influence of these two factors. One was advanced by Smee and is summed up in the statement: current density and concentration of the bath determine by their relative proportions the quality of the metal. The second view was given by F. Kick as follows: the quality of the galvanic deposit is dependent upon the composition of the electrolyte and independent of the current density.

Smee, upon the basis of his numerous investigations, comes to the following conclusions:

1. The metal is separated out in a non-homogeneous form (powdery, spongy, or sandy) if the current strength is so great that evolution of hydrogen occurs simultaneously with the deposition of the metal.

2. The metal is separated out in a coarsely crystalline form if the current strength is far from being sufficient to cause evolution of hydrogen.

3. The metal appears as a tough, solid, fine-grained deposit if the current strength is as great as possible, but not strong enough to cause evolution of hydrogen.

Smee therefore concludes that by the application of proper current density it is possible to obtain deposits having certain properties from baths of almost any concentration.

H. Meidinger (Dingler p. J. 218, 219) reviews the conclusion of Smee and adds this statement: "The relation of the current density to the concentration of the solution is a constant for a determined quality of the precipitate, but the limits are not very sharply defined. If a deposit of certain properties is obtained from a concentrated bath a similar precipitate might be obtained from a bath of half the concentration by half the current strength, from a bath of one-third the concentration by one-third the current strength, etc."

Hübl made extensive experiments to find the most suitable relations for producing the best precipitates. His preliminary experiments on a small scale, to determine the appearance and the brittleness of the precipitates, were carried out as follows:

## HÜBL'S INVESTIGATIONS.

The copper sheets used as electrodes were 50 mm. wide, 100

| Current Density. | Copper solution. | Appearance of the precipitate from the 5% Bath. | Appearance of the precipitate from the 20% Bath. | Cohesion of the Deposit from the 5% Bath. | Cohesion of the Deposit from the 20% Bath. |
|---|---|---|---|---|---|
| 0.20 | Boiled with copper carbonate. | Very coarsely crystalline. | As in the 5% bath. | Very fragile and brittle. | Worse than in the 5% bath. |
| 0.40 | | Coarsely crystalline. | | Somewhat fragile and brittle. | Very fragile and brittle. |
| 0.80 | | Somewhat coarsely crystalline. | | More or less good. | Very fragile and brittle. |
| 3.00 | | Hydrogen evolved. | Very finely granular; crystalline structure not recognizable. | | Faultless. |
| 0.20 | 2% of sulphuric acid added. | Finely crystalline. | Same as 5% bath. | Somewhat brittle and fragile. | Same as 5% bath. |
| 0.40 | | Ditto. | | Good. | |
| 0.80 | | Very finely crystalline. | | Good. | |
| 1.20 | | Hydrogen evolved. | Extremely finely granular. | | Faultless. |
| 4.00 | | Ditto. | | | Faultless. |

mm. long and held at a distance of 20 mm. apart by suitable supports. The cathode was silvered and slightly iodized in order to facilitate loosening of the precipitate. A glass beaker filled with the experimental solution was brought under the electrodes and raised until the latter dipped 50 mm. into the solution. Daniell or Bunsen cells served as the source of current, a circular rheostat in the circuit serving to regulate the current strength. When experiments were to be made with agitated baths the desired agitation was obtained by the bubbling in of air.

Two pairs of electrodes were always in the circuit, one pair dipping into a 5 per cent., the other into a 20 per cent., solution of copper sulphate.

At first so-called neutral solutions (boiled with copper carbonate) were electrolyzed, using various current densities, the solution being replaced after each experiment in order to produce no irregularity by the change in the composition of the bath.

NEUTRAL SOLUTIONS.

It follows from these results that, using a so-called neutral solution and a smaller current density in a 5 per cent. bath, better precipitates are obtained than in a concentrated solution, while the appearance of the metal in both cases is the same. The cause of this phenomenon has already been alluded to. The addition of sulphuric acid hinders the formation of large crystals. There are therefore obtained with small current densities very finely granular, tough deposits whose texture and behavior in bending are independent of the concentration of the solution.

The more or less crystalline texture appears as well with so-called neutral as with acid baths, depending entirely upon the current strength used. The coherence of the metal which is to some extent shown by its behavior on bending agrees completely with the development of the crystals in acid baths, but in neutral solutions appears to be determined almost entirely by the basicity of the solution.

In order to obtain a useful deposit the current density used should not exceed a maximum already stated, as determined by the concentration of the bath; within this limit, however, the current density is the only determining factor of the texture and the properties depending upon the texture.

### THE ACTION OF ADDITIONS.

The reason why only finely crystalline deposits are obtained when acid is added has so far not been explained. Meidinger attempted an explanation, according to which the cause was the indirect separation of the metal, but in this case similar influences should be exerted by other substances. If to a 10 per cent. so-called neutral bath there is added 10 per cent. of sodium sulphate, there must in this case according to the conductivity of the latter, certainly be a large part of the copper separated out indirectly by the sodium. But with a current density of 0.8 of an ampere such a solution gave a quite as coarsely crystalline and fragile deposit as without this addition.

### ADDITION OF SULPHURIC ACID.

Concerning the quantity of the sulphuric acid added, experiments on this point show no difference in the texture of the precipitate when 2 to 8 per cent. of acid was present.

### TENSILE STRENGTH.

The determination of accurate values for the tensile strength of galvanoplastic deposits is attended with extraordinary difficulties and in spite of serious attempts it was not found possible to obtain complete correspondence between the numbers found and the variations in the method of producing the deposit.

A great difficulty is primarily in the production of perfectly faultless plates of dimensions large enough to make the tests on them. Irregularities in the growth of the precipitate (the formation of copper granulees which when removed show a changed structure at the point where they have been removed) influences self-evidently the numbers found by the testing machine.

Experience has, however, shown that copper of smaller strength is deposited from old baths. The reason of this phenomenon could not be explained, since the chemical analysis of the old baths with the exception of a trace of cuprous salt, showed no differences from the new baths just going into use. It appears highly probable that the turbidity of the baths which have been used, caused by the particles of anode slime in suspension, exert a prejudicial influence on the precipitate. It is also, however, very

probable that substances coming from the lining material of the cell, as lacquer upon the back of the cathodes, contaminate the baths.

For this reason the following results, which have been taken from copper specimens precipitated from long used baths, do not represent the best obtainable results and can on these grounds only be regarded as values for comparison among each other.

The method of the production of the specimens was as follows: A layer of copper 0.8 to 1 mm. in thickness was deposited by a carefully measured current from a dynamo machine, upon a smooth silvered copper plate of proper dimensions, covered on the back with an asphalt varnish. The current density was calculated from the current strength and the size of the plates. Two sheets each 50 mm. wide were cut from the middle of the plate in a determined direction and subjected to a tensile test.

### TENSILE STRENGTH TESTS.

The table in the appendix contains the average values gathered from two series of investigations.

Considering first the values for each test obtained from baths of similar concentration, the following conclusions may be drawn:

1. The absolute strength increases with the current density. With not quite pure baths the differences are smaller than when using freshly made up solutions. The relatively highest values appear to be obtained with a current strength of 2.2 to 3 amperes; with still higher densities the absolute strength decreases. This is explained by the fact that 4 amperes is in the neighborhood of the practically allowable current density, and at this strength the tendency becomes manifest to separate out sandy copper. This phenomenon will also occur in a short time if the agitation of the bath is ceased and it is allowed to stand quiet.

2. The elastic limit and elongation show a maximum with current strengths of 1.0 to 1.5 amperes.

3. The toughness of the metal, represented by the elongation at rupture, decreases with increase of current strength.

The maximum value lies below a density of 0.6 ampere, yet it might be supposed that with very small densities the toughness would decrease because of the appearance of a more crystalline structure.

4. The hardness increases with the current density. It is to be observed that the method of determining hardness gives correct results with thick plates, but that with thin sheets deformation may occur, making the method of the determining of the hardness unreliable.

Discussing the relations between the above properties and the concentration of the bath it may be observed that:

1. The absolute strength is almost independent of the composition of the bath. The results of the series of experiments with freshly made up baths are very plainly different from those with old baths; but in each group similar current densities correspond to nearly equal tensile strengths, independently of what concentration was used in the bath. These values are graphically set forth in connection with the table.

2. The elastic limits and the elongations show undoubtedly the influence of the concentration of the bath; since as the latter decreases these physical values decrease also.

3. The values for the toughness show such irregularities that the correspondence between it and the concentration of the bath is scarcely to be recognized. Tests 10 and 11 in particular are quite isolated from the others. The other values allow of conclusions respecting the variation of toughness with current density alone, but there are some striking relations between the properties of the precipitate and the ratio of the concentration of the bath to the current density.

The results are given further on. The following additional explanations may be added:

The elastic limit given under 1 and 2 is expressed by the number of kilograms which a bar of one square centimeter cross-section can support without producing a permanent elongation of 0.00001 or 0.0001 respectively of its length.

The hardness is expressed by the length of a nick which is produced by a chisel upon which a certain weight is allowed to fall. The longer nick corresponds therefore to a relatively softer copper, and conversely.

The sheets distinguished by ↕ are taken from vertical hanging plates in a vertical direction. Those distinguished by ↔ are cut in a horizontal direction. There was thus obtained as relative hardness:

No. 15 = 19.4 from a 20% bath and 4.00 amp/sq. dm.
No. 18 = 19.4 " " 15% " " 3.23 "
No. 20 = 17.2 " " 10% " " 1.50 "
No. 21 = 19.7 " " 5% " " 1.30 "

It is to be remarked that defects in the material would be of great influence upon the length of the sheets after rupture, which circumstance may be the cause of some of the irregularities which the values of the toughness show.

From these investigations it must be concluded that practically the current density, partly also its relation to the concentration of the bath, determine the strength and elasticity of the galvanic deposit. If the entire electrolytic process proceeded perfectly it is highly probable that the qualities of the deposit would depend upon the current density only; this would determine the crystalline texture of the product and the mechanical properties would be in correspondence with it. But since without doubt secondary processes occur during the electrolysis, the intensity of which depend upon the relation of the current density to the concentration of the bath, the latter factor must also influence the qualities of the precipitated metal.

For practical purposes the following rules may be developed from the above facts:

1. If copper of the greatest tensile strength and hardness is to be deposited and less weight is laid upon great toughness, high current densities of 2 to 3 amperes per square decimeter should be used. The electrolyte must in this case evidently be as concentrated as possible (20 per cent.).

2. If copper of the greatest possible toughness is desired, and hardness and strength are of less importance, current densities of 0.6 to 1 ampere are suitable. The electrolyte would be a 16 to 18 per cent. solution.

The absolute tensile strength of a good galvanic deposit approximates that of cold-hammered plate and its elastic limit in some tests has gone considerably higher.

As far as toughness is concerned the galvanic deposits are considerably superior to the rolled metal. This is very well deserving of notice.

As is shown in experiment No. 12, the cohesion of the precipi-

tate upon a vertical hanging plate is not the same in all directions. Tensile strength, elastic limit and especially the toughness are greatest in a vertical direction. This circumstance is only to be explained by the orientation of the crystals, which is influenced by the upward flowing current of electrolyte. This fact is also of practical value in that it is sometimes desirable to put the articles being produced in such position in the bath so as to produce the above effects in certain desired directions. Copper plates for engraving are therefore always to be produced in such manner that the strongest cohesion of the metal lies in the direction along which the plate passes in the printing press.

Experiment No. 23 is made with a plate produced with the greatest care in a Daniell trough apparatus. The apparatus was charged with the so-called English vitriol; the measured current strength was 0.25 ampere. The absolute tensile strength and toughness are in fact lower than those made with dynamo-electric machines, yet this precipitate is to be regarded as a particularly fine one in view of the manner in which it is made.

Appendix V of Hübl's "Original-Abhandlung" shows the deformation which different precipitates suffer under the tensile tests. Tests 2 and 3 are well worthy of notice; for they have a higher elastic limit than refined copper, and yet show a surprisingly good behavior on rupture.

Foerster and Seidel[1] took these questions up later and obtained results in complete accord with those of Hübl. They discovered, however, an important new factor; *viz.*, the influence of the temperature of the electrolyte upon the physical properties of the copper. The following values were found:[2]

| Temperature of the Electrolyte in °C. | Average bath-tension. Volts. | Relative tensile strength[2]. | Toughness Per cent elongation at rupture. |
|---|---|---|---|
| 20 | 0.32 | 2.15 | 9.12 |
| 40 | 0.25 | 2.67 | 26.00 |
| 60 | 0.20 | 2.69 | 13.50 |
| Drawn wire from Mansfield electrolytic copper. | | 2.83 | 31.00 |

It appears therefore that the temperature of 35 to 40° C. is the

[1] Zeitschr. f. Elektrochemie **5**, 508 et seq.

[2] These numbers represent the length of a wire of the metal in Kilometers which will support its own weight. These tests were made at the Mechanical Institute at Dresden by Dr. Hartig.

most suitable, while an elevation above this causes a decrease in tensile strength of the copper. The reason of the favorable action of the higher temperature upon the structure of electrolytic copper was not definitely known. Foerster[1] is of the opinion that the temperature of the solution determines the size and regularity of the small crystals of the deposit and thus determines its structure; he conducted two experiments in a bath which contained an amount of Glauber salt equivalent in amount to the copper sulphate present, along with the usual amount of sulphuric acid.

| Temperature of the electrolyte in °C. | Tensile strength (relative). | Toughness. Per cent elongation at rupture. |
|---|---|---|
| 20 | 2.46 | 15.20 |
| 40 | 1.96 | 10.82 |

From this it is to be concluded that when alkaline sulphate is added, the increased temperature influences unfavorably the physical properties of the copper, while on the other hand, the results at 20° C. were better with the addition of alkaline sulphate than without it.

The galvanoplastic baths in ordinary use at present are made up according to the principles above explained, and Hübl's and Foerster's investigations, which furnished the foundation for the present stage of development. Later investigations have been concerned mostly with increasing the speed of deposition of the copper precipitate and the copper baths in practical use at present have been modified according to the principles discovered by Carl Polenz and the author,[2] and give precipitates much more quickly and yet without a deterioration of the quality of the cathode copper.

### RAPID DEPOSITION.

While Carl Polenz used a solution containing 350 grams of copper sulphate in a liter of water and warmed to 30° C., the author used a bath of the following composition:

| | |
|---|---|
| Water | 1 liter |
| Copper Sulphate | 250 grams |
| Sulphuric acid | 7.5 grams |
| Alcohol | 5 grams |

[1] Zeitschr. f. Elektrochemie 5, 511.

[2] Wilh. Pfanhauser: "Elektroplattierung, Galvanoplastik und Metallpolierung," 4th Ed., 1900.

This bath possesses a specific resistance of 1.6 ohms and a temperature coefficient of 0.0096. The temperature was about 20° C.; yet higher temperatures, such as are produced by high current densities, up to 10 amperes per square decimeter, are quite harmless if they do not exceed 30° C.; in fact, they exert a favorable influence on the precipitate. The electrolyte was kept in motion by an air blast, thus furnishing concentrated copper solution constantly to the cathode and at the same time cooling the solution so as to dispense with the use of cooling water.

OLD BATHS.

The bath formerly used for galvanoplastics was composed of

| | |
|---|---|
| Water | 1 liter |
| Copper sulphate | 200 grams |
| Sulphuric acid | 30 grams |

Specific resistance 0.93 ohm, temperature coefficient 0.0112.[1]

POWER REQUIRED FOR COPPER PRECIPITATION.

If the relative currents are compared, as required for the usual bath and for the rapid deposition bath of Pfanhauser, the power required to deposit one kilogram of copper, the distance between the electrodes being 10 centimeters, is as follows:

| Current density in amperes per square decimeter. | In ordinary galvanoplastic bath. Horsepower—Hours. | In Pfanhauser's rapid galvanoplastic bath. Horsepower—Hours. |
|---|---|---|
| 0.5 | 0.67 | .... |
| 1.0 | 1.34 | .... |
| 1.5 | 2.01 | .... |
| 2.0 | 2.68 | 4.60 |
| 3.0 | .... | 6.90 |
| 4.0 | .... | 9.20 |
| 5.0 | .... | 11.50 |
| 6.0 | .... | 13.80 |
| 7.0 | .... | 16.10 |
| 8.0 | .... | 18.40 |
| 9.0 | .... | 20.70 |
| 10.0 | .... | 23.00 |

The power requirement is proportional to the specific resistance of the electrolyte as long as no polarization phenomena appear, that is as long as no counter electromotive force complicates the calculation. If the Pfanhauser rapid deposition bath is kept in use for a long time the electrolyte becomes impoverished in free sulphuric acid and therefore acid must be added from time to time.

[1] As measured by the author.

# IV. BEHAVIOR OF COPPER ANODES.

## ANODE SLIME.

In this field Hübl has also made some skillful observations, and Foerster also has given extensive communications on anode slimes in the baths. Max Herzog von Leuchtenberg has also written concerning the slime residue. Commercial copper, not electrolytic, may contain impurities of the most different elements, of which I may mention, Au, Ag, As, Sn, Pb, Fe, Ni, S, etc., which are usually known outside of the copper refinery.

But the electrolytically produced copper, if it has not been rolled before being used as an anode, also furnishes a reddish slime which was investigated as early as 1875 by Kick.[1] He determined that it contained about 60 per cent. of metallic copper and 40 per cent. of cuprous oxide, $Cu_2O$.

Hübl does not agree with Kick for he writes: "If what F. Kick observed is correct, a part of the $SO_4$ radicle liberated at the anode would have to form free sulphuric acid and oxygen. In that case the content of the bath in free sulphuric acid would increase after long use." Since the quantity of the slime formed when using electrolytic copper as anodes is in considerable amount, it was interesting to further investigate this phenomenon.

As far as commercial copper plates were concerned the results obtained substantiate completely those of Leuchtenberg. The quantity of black slime produced depends almost solely upon the purity of the metal and is quite small when using the better grade of copper at present found in commerce. Using electrolytically produced anodes, however, there appears to be produced a much larger quantity of a light brown slime which was found to be completely free from foreign metals. After washing and drying there remains a heavy, dense, brittle mass, readily taking a coppery lustre when polished. Under the microscope it was seen to be almost entirely composed of more or less well preserved copper crystals.

[1] Dingler Pol. J. 218, 219.

### COMPOSITION OF THE ANODE SLIME.

Using pure anodes deposited electrolytically, repeated chemical analyses of the residues showed them to consist only of pure copper. The method of Hampe,[1] the determination of the loss of weight by ignition in a current of hydrogen, was used for the determination of the oxygen present in the residue. In two tests no oxygen at all could be found, and therefore $Cu_2O$ could at most only have been present in traces. If the washing and drying of the copper slimes has not been done with the proper care it begins to take a yellow color and in that case considerable quantities of $Cu_2O$ can be found. A test of a partly oxidized slime of this nature showed a content of 4.7 per cent. of $Cu_2O$.

The residue from galvanic deposited anodes consists therefore of microscopically small copper crystals which have the property when used as an anode of remaining unaltered. It is highly probable that they really exist in a passive state which may be due to an extremely thin coating of cuprous oxide, $Cu_2O$, not detectable analytically. Only galvanic deposited copper shows this phenomenon, which may be explained by its quite characteristic crystalline structure.

### INFLUENCE OF THE ANODE SLIME ON THE PRECIPITATE.

This copper slime thus formed is a highly undesirable material for the galvano-plater, since it causes a turbidity in baths which are agitated, becomes entangled in the precipitated copper, causes rough surfaces and lowers the cohesive strength of the metal.

On these grounds it is desirable to use commercial rolled copper plates in preference to the electrolytically deposited.

All the observations so far made concerning anode slime relate to acid baths. When using the so-called neutral baths the formation of cuprous oxide, $Cu_2O$, can be actually observed, particularly when high current densities are used. The anode in this case becomes at places plainly reddish yellow and under this condition the bath shows a change in its acidity after the electrolysis.

Foerster also finds only a small amount of cuprous oxide, $Cu_2O$, and determined that it consisted likewise of small crystals of pure copper. He explained the formation of these small crystals by

[1] Zeitschr. f. anorgan. Chemie 13, 202.

the increase in the concentration of the solution in the neighborhood of the cathodes which were surrounded loosely with parchment paper; and by the tendency of the anode copper to furnish copper ions to the solution, producing in the immediate vicinity of the anode cuprous sulphate, $Cu_2SO_4$, which decomposed spontaneously into cupric sulphate, $CuSO_4$, and the crystalline precipitate of copper.

$$2\,\overset{+}{Cu} = \overset{++}{Cu}$$

$$\overset{++}{Cu} + Cu = \overset{+}{Cu_2}SO_4,$$

$$\overset{+}{Cu_2}SO_4 = \overset{+}{Cu}SO_4 + Cu.$$

POLARIZATION PHENOMENON.

The author has observed that when using envelopes of parchment paper, silk, etc., around the anode the current strength falls soon after closing the circuit, instead of remaining constant, and in this case reaches constancy only at a small fraction of an ampere. But since it is desirable at times to keep the anode slime out of the body of the electrolyte, particularly when the baths are agitated, in order not to interfere with the physical properties of the precipitated copper, I began investigations to find a suitable envelope which would be close enough to retain fine slime and on the other hand sufficiently porous to keep down the tendency to increased concentration inside the envelope, which occurs particularly with high current densities. Flannel not too tightly woven was found to be the only suitable material. Using current densities of even 8 amperes per square decimeter and envelopes of this material, there was no sign of the falling off of the current after closing of the circuit and the solution remained clear of slime even when the so much feared electrolytic anodes were used. In this manner, plates 4 to 5 millimeters in thickness were produced, using current densities of 8 amperes per square decimeter and having only very small unevenness on the depositing surfaces.

# V. CONSTANTS OF THE BATH AND CALCULATION OF THE AMOUNT OF DEPOSIT.

The operation of plants for the electrolytic manufacture of metallic objects must be so arranged, it will be admitted, that even the workmen may be able to determine at once whether their baths are working or not. For this reason, each bath must be supplied with an ammeter and a voltmeter, as well as, when necessary, a regulating resistance either in series or in parallel with the bath; we will speak later of this. Since the ordinary workman having charge of the bath cannot be expected to be able to calculate specific bath resistances, current density, etc., it is necessary to give him precise data concerning the proper indication of his instruments, from which he can draw conclusions concerning the correct working of his bath. On the contrary, the constants of the bath should be known to the person in charge, and I will therefore at this place recapitulate briefly the methods of determining them.

DETERMINATION OF THE SPECIFIC RESISTANCE.

In Fig. 1, AA, indicates a stretched wire of "constantin" serving as a measuring wire and provided with a millimeter scale.

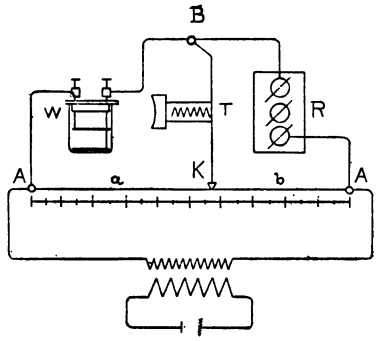



Fig. 1.

From the point A a conductor leads to the Arrhenius cell W, which contains the electrolyte to be investigated and whose other pole is in connection through B with the plug rheostat R, and

through it to the other end A, of the measuring wire. Between the point and the movable wire contact K there is inserted a Bell telephone T, which gives a sound by means of the alternating current generated in the induction coil, so long as a current flows through the telepone. By suitably changing the resistance in R and sliding of the contact K, the current through the telephone can be brought to zero when the potential fall through BR is equal to the potential fall through the other side of the circuit. The relation of resistance at this point is therefore

$$\frac{a}{b} = \frac{W}{R}$$

the latter reading being the relation of the distances AK and $A_1$, K, respectively, as measured in millimeters, and on the further assumption that the measuring wire has a constant resistance for uniform distances on the scale.[1] (For the most accurate work the measuring wire should be calibrated). From the above proportion the resistance of the cell W between the two platinized electrodes of the Arrhenius vessel is calculated, that is

$$\text{Resistance of cell} = \frac{a}{b} \times \text{Resistance of plug rheostat.}$$

W being known, the determination of the specific resistance of the electrolyte, $R_s$, taking as a practical unit[1] a cube of the fluid one decimeter on a side, may be found by dividing R by the resistance capacity K of the measuring vessel, in which K is the ratio of the length to the cross-section of the electrolytic resistance measured, this proportion being called the resistance capacity of the measuring vessel. This proportion can be gotten by measusement, or by an experimental determination by placing in the vessel a fluid of known specific resistance, and measuring the resistance of the vessel, so that the actual resistance divided by the specific resistance of the fluid gives the ratio K for the vessel used.[2]

[1] See Kohlrausch and Holborn.

[2] The specific resistance of fluids is usually expressed in the tables as that of a centimeter³ of the liquid, which value is ten times the value $R_s$ chosen as the unit by Mr. Pfanhauser and attention should be paid to this difference when using Pfanhauser's formula and taking the specific resistance from the ordinary tables.—TRANSLATOR.

As an example, the resistance K of an Arrhenius cell was found to be 0.2, and the actual resistance of the unknown fluid was 0.3 ohm, from which the specific resistance of the unknown fluid was calculated to be $\frac{0.3}{0.2} = 1.5$ ohms.

For further details to be observed in this measurement, such as the choice of the calibration fluid, choice of the form of the measuring vessel, etc., reference is made to the work of Kohlrausch and Holborn, "Das Leitvermogen der Elektrolyte."

CALCULATION OF THE BATH TENSION.

When one knows the specific resistance of the electrolyte, then, if the distance of the electrodes apart and their sizes are carefully measured, the total resistance of the bath $R_b$ is equal to the specific resistance multiplied by the length of the bath between the electrodes and divided by its cross-section.

$$R_b = \frac{R_s \times l}{s}$$

In this formula s is the active cross-sectional area of the electrolyte and $l$ the mean distance apart of the electrode surfaces from each other expressed in square decimeters and decimeters respectively. In order to send through the bath with a resistance $R_b$, a current of A amperes, a potential difference V volts is necessary. If $\frac{A}{s}$ is assumed to be the current density per square decimeter (ND/100) and if the alteration of the resistance with the temperature is taken into account, we have the relation

$$V = AR = A \cdot R_s \frac{l}{s}$$

$$V = ND_{100} \cdot l \cdot R_s (1 \pm \alpha t)$$

If the counter electromotive force $V_a$ enters into the galvanic process, its amount (expressed in volts) appears on the right side of the above equation; so that the expression for the total bath tension will be

$$V = ND_{100} \cdot l \cdot W_s (1 \pm \alpha t) + V_a.$$

GROWTH IN THICKNESS OF GALVANIC DEPOSITS.

To calculate the growth in thickness of galvanic deposits the

current density used and the duration of the electrolysis are the determining factors. A third factor is the electrochemical equivalent of the metal being precipitated from the solution used. There are, for instance, two different rates of precipitation of copper according to whether it is precipitated from cuprous or cupric salt solutions. According to Faraday's Law, 96,540 coulombs separate a gram-equivalent of metal, or in round numbers, 26.8 ampere-hours are necessary, as a practical unit.

So the amount of copper precipitated by an ampere-hour is 3.272 grams from a cuprous solution and 1.186 grams from a cupric solution.

The amount of metal precipitated in a given time $t$ in hours by a given current A in amperes and with an efficiency in precipitation $e$ expressed in percentage, would be, calling the amount of metal precipitated by one ampere-hour W.

$$W = W_1 \cdot A \cdot t \cdot \frac{e}{100}$$

[This value of W, would be 3,600 times the usual electrochemical equivalent of the metal; that is, the amount precipitated by one ampere-second or one coulomb.—*Translator.*]

Calling D the specific gravity of the precipitated metal, the thickness T in millimeters of the metal deposited on the cathode of surface S

$$T = \frac{W_1 \cdot A \cdot t \cdot e}{S \cdot D \cdot 1000} = \frac{W \cdot (ND_{100}) \times t \cdot e}{D \cdot 1000} \; m\,m.$$

From this equation any single value can be easily obtained; thus for instance the time in which a given current density must act in order to obtain a deposit of a given thickness

$$t = \frac{T \cdot D \cdot 1000}{W_1 \cdot (ND_{100})\, e}$$

The current density to be used (ND/100) will be expressed by the formula

$$N\,D_{100} = \frac{T \cdot D \cdot 1000}{t \cdot W_1 \cdot e} \text{ amperes.}$$

The subsequent tables contain numerous examples and references may be made to them.

# VI. INDUSTRIAL PLANTS.

Before passing to the practical operation of the different processes, I will give a few further fundamental points concerning the equipment of the plants, such as may not be unwelcome to the manufacturer.

### SOURCE OF CURRENT.

First of all concerning the source of current, there is seldom above 15 volts tension needed at the dynamo-machine because greater tensions are unsuitable from the danger of the ground connection which may be made through the tanks. We are dealing also with well conducting solutions and during the manipulation of the cathodes, their taking out and putting in, naturally some of the fluid is spilled and may cause ground connections.

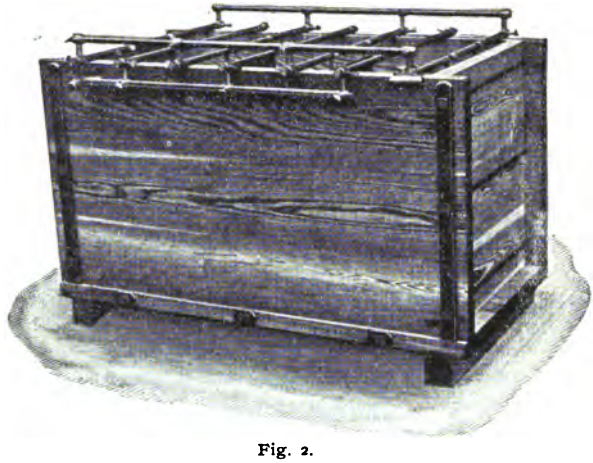


Fig. 2.
TANKS.

The tanks for electrolytic use are almost universally made of larch or pitch pine wood, vessels of earthenware or cement being seldom used. The wooden vessels have as their greatest advantage the slight danger of being broken, and besides auxiliary apparatus can easily be fastened to wooden tanks; for instance, stirring apparatus and the like.

Fig. 2 shows a wooden tank such as is used in the manufacture

of metallic papers. Such vessels are usually rated according to contents and the following table gives the approximate prices which the various sizes cost, on the average, per unit of contents.

| Capacity. | Cost per liter of capacity. |
|---|---|
| 100 liter | 7.5 cents |
| 100—150 | 5.0 " |
| 150—200 | 4.5 " |
| 200—250 | 4.0 " |
| 250—300 | 3.5 " |
| 300—400 | 3.0 " |
| 400—500 | 2.7 " |
| 500—600 | 2.5 " |
| 600—800 | 2.2 " |
| 800—1000 | 2.1 " |
| Over 1000 | 1.7—2.0 " |

It is recommended to set all tanks on a cement floor so that they do not warp and leak as they would do on a wooden floor.

### CONNECTING UP OF THE BATHS.

On a large scale when certain duplicate objects are being produced, a series connection of the bath is to be recommended for many reasons, because in that manner the production becomes more uniform. When connecting in series, there is an assurance that the cathodes all receive the same amount of metal, will all be ready at the same time, and must be of similar quality. It is self-evident that the electrode surfaces in the several baths must be alike.

If there are considerable differences, however, in the sizes of the objects when many small pieces are to go into one bath, it is necessary to use parallel connection of the baths, or regulating resistances connected up in parallel to each one of the baths which are in series. These rheostats, in combination with the resistance of the bath thus provide a normal resistance of the cell unit.

A schematic diagram of such plants is shown in Fig. 3. DM is the dynamo-machine furnishing current, AM is the principal ammeter. The nine baths are divided into three groups connected in series, each group consisting of three baths in parallel. Each series has a regulating resistance RWI, RWII, and RWIII, respectively, connected in parallel.

If, for instance, R is the total resistance of a single bath, $R_1$ that resistance which exists in a similar bath with a smaller cathode surface, then it is necessary to put in parallel with this series a resistance $R_2$, which in connection with the resistance $R_1$ will give a normal resistance R.

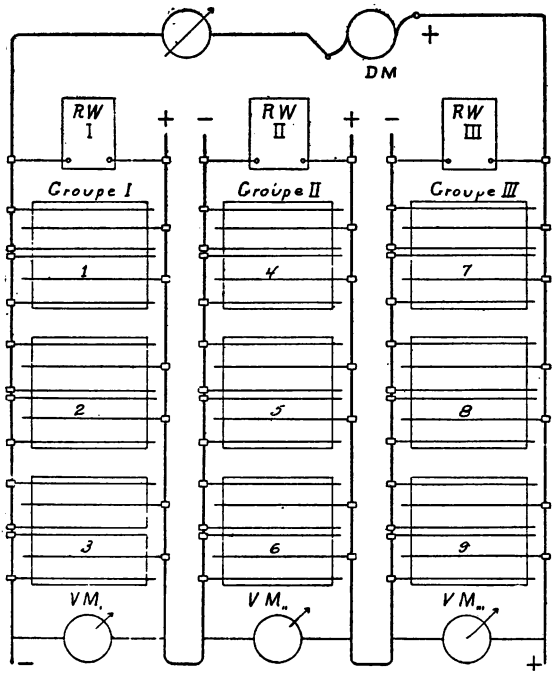



Fig. 3.

The method of connection must therefore fulfill the condition expressed by the formula

$$R = \frac{R_1 + R_2}{R_1 \times R_2}$$

A voltmeter attached to the ends of the rheostat shows to the workman whether the adjustment has been properly made, since the normal current density will be present in the bath when the voltmeters of the separate baths are alike. If the voltmeter reads below the normal bath tension, then too great a current is passing

through the rheostat and too small a current through the bath and the latter is working with too small a current density; in this case the resistance of the rheostat should be increased until the voltmeter indicates the normal bath tension.

PARALLEL CONNECTING OF THE BATHS.

When the baths are connected in parallel, the rheostats are connected in series with the baths so that the bath-current goes through the rheostat. This provides a means of reducing the voltage of the system down to a normal bath tension or of making the bath tension smaller in order to produce a normal current density when there are smaller cathode surfaces in the bath, which disturb the relation between the anode and cathode surfaces.

The regulating resistance then absorbs the voltage $V_s$-v; that is, it causes this drop of potential when the bath current passes through it. Its maximum resistance is therefore:

$$R\ (max) = \frac{V-v}{A\ (min)}$$

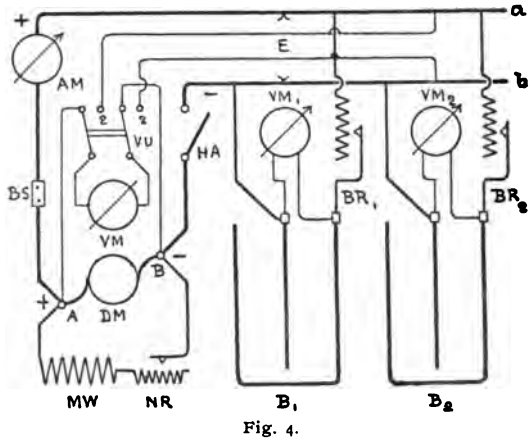



Fig. 4.

Fig. 4 shows this method of connecting used for two baths. $BR_1$ and $BR_2$ are the bath-current regulators for the baths $B_1$ and $B_2$. The voltmeters $VM_1$ and $VM_2$ are in parallel with the electrodes. a and b are the main conductors, DM the central dynamo, MW the shunt winding, NR the field regulator, BS the lead fuse,

AM the main ammeter, HA a single pole hand switch, and VU a voltmeter switch for the voltmeter VM. The voltage of the system, V, measured by placing the voltmeter switch on the arrestment 2, is held constant by the shunt regulator, and the bath tension is adjusted by the regulator $BR_1$ and $BR_2$.

### THE CONDUCTORS.

It naturally can not be within the scope of this work to treat of the calculation of the conductors. I will limit my observations to what I regard as normal: the drop of potential in the conductors should not be greater than 7.5 per cent. of the voltage at the dynamo terminals, whether either parallel or series connection is used. The plant with series connections necessarily works better from a financial standpoint because the cross-section of the conductors is much smaller, also the contact surfaces at the joints of the conductors may be lighter.

On the other hand, the insulation is simpler with parallel connecting and therefore in many plants a mixed connection such as is shown in Fig. 3 has been found most suitable.

# VII. PARTICULAR DEVICES FOR SPECIAL PURPOSES. PRODUCTION OF UNIFORM DEPOSITS.

### DISTRIBUTION OF CURRENT LINES.

If the current is allowed to pass from an anode of any size to a smaller cathode, without taking particular precautions, it is often found that the edges and such parts of the cathode which hang closer to the anode are more heavily coated with deposit than the other parts. The explanation of this is as follows: the separate surface elements of the cathode and those of the anode form in combination with the corresponding cross-section of the electrolyte a total resistance R which is formed of the parallel single resistance elements $r$. According to Kirchoff, however, the total current A must distribute itself in proportions corresponding to the conductivities of the separate resistance elements. With equal distances between all of the cathode-surface elements and the corresponding anode-surface elements (assume these elements 1 square centimeter each), there will result an equivalence of the separate resistance elements, giving them the values;

$$r = \frac{l \times 100}{k \times s}$$

the result being in ohms if $l$ is the distance of the electrode surface elements from each other, in decimetres, $k$ is the conductivity of the electrolyte per decimetre,[3] and $s$ is the cross-section (say one square centimeter) of the conducting fluid.

In case that the anode as well as the cathode form the end surfaces of the trough and are parallel to each other and reach to the surface of the fluid, all the resistance elements in the fluid are equal. Or if it is possible that there is a certain cross-section of electrolyte above the edges of the cathode, then current lines diverge into this space and concentrate down upon the edges of the cathode. The consequence is that the sum of these lines

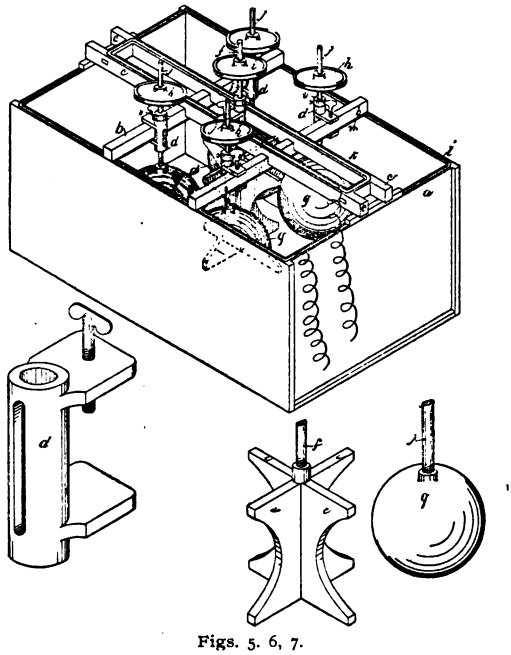
$$\Sigma \frac{l \times 100}{k \times s}$$

will increase the current density upon the cathode edges, whereby an inequality of the rate of growth takes place.

The case is similar if projecting parts of the cathode or anode reduce the length $l$ of the resistance elements. This results in increasing the current density on the electrode surface elements concerned and increases the influence of electrolysis upon cathode or anode.

### UNIFORM DEPOSITS.

Fletcher[1] obtained uniform deposits by rotating the cathode and arranging the anodes at a certain distance from it. It may be remarked that Fletcher's method can be improved if the various distances for the anodes are worked out graphically.



Figs. 5. 6, 7.

Engelhardt[2] made the further improvement by eliminating the errors which could not be avoided by rotating the cathode alone, by rotating the anode as well as cathode. Thus, by varying at

1 American Patent, 485, 343—Lum. El. 1892, 47, 32.

American Patent 544, 668, Aug. 20, 1895. See also Zeitschr. f. Elektrochemie 2, 408.

times the initial velocity of rotation, the average current density on all parts of both cathode and anode can be kept alike, whereby a uniform growth of the deposit and a uniform solution of the anode would be obtained.

The apparatus proposed by Engelhardt for obtaining these ends is shown in Figs. 5, 6, and 7.

The contact strips *l* are placed upon the edge of the decomposition cell *a*. Upon these rest the cathode carriers *b* of non-conducting material having metallic strips *m* underneath. At right angles above them are the anode carriers *c*, which are provided with the conducting strips *k* on their upper surface. The electrodes *e* and *g*, fastened to rods *f* and *j*, are hung to their supports by the clamps *d* and so connected with the conductors.

The collars *v* are movable upon the rods *e* and *g* and can be clamped by screws and so hold the electrodes in the guides *d*. The electrodes can be rotated by means of the rope pulleys *i* and *h*.

## PROCESS OF BAUER.

J. G. Bauer[1] patents the following process for the manufacture of curved bodies which must be precipitated upon moulds having the corresponding projections.

*Patent Claims.*

1. A process for the production of uniform galvanic deposits upon non-conducting bodies, characterized by having metallic chains inserted into the cores, the links of which appearing at the surface of the core form points of attachment for the galvanic precipitate..

2. The use of the principles of Claim 1 applied to cast articles of wax, gypsum, etc., consisting of inserting through these bodies metal wires provided with heads or enlargements, in such manner that one end of the metal wire appears at the upper surface of the body while the other end is connected with the main current conductor.

## PROCESS OF ANDERSON.

Anderson[2] worked similar to Fletcher, surrounding a rotating cathode core by anodes arranged around it concentrically as anode strips.

[1] German Patent 65, 819, Feb. 6, 1892.
[2] American Patent 534, 942, Feb. 26, 1895.

## WURTTEMBERG PROCESS.

The superintendent of the Württemberg[1] Metal Ware Works made an important advance in this special line, useful in case that a non-uniform division of the precipitate was desired, where for instance certain projecting parts of the finished article were desired to be more thickly coated. This is obtained by placing in the bath between the article and the anode, plates of insulating material, such as glass, etc., which are provided with openings and result in largely cutting off the current from the parts which are covered and increasing the current passing to the parts immediately behind the openings, so as to produce at will a non-uniform distribution of the current.

These plates may be called screens or current-line deflectors. If the opening in the distributor is for instance circular, then the current lines form approximately a paraboloid of revolution and the projection of the latter upon an article gives the desired distribution upon the cathode. Self-evidently, the projection surface upon the cathode varies with the distance of the deflector from it and if the latter is at a great distance, the projection becomes blurred and disappears.

The process is protected by the following patent claim:

### *Patent Claim.*

Process for the simultaneous obtaining of galvanic metallic deposits of varying thickness upon the same object, produced by arranging between the latter and the anode freely hanging plates of insulating material.

### *Extension of the Process.*

These cleverly designed aids can, as has been proved by the inventor, be used in order to produce heavy precipitates upon the deeper lying parts of the mould, in the production of curved objects: this is done by arranging the perforated shields before the cathode with the opening so arranged that the resistance capacity of the elements of the cathode surface at the deeper lying parts is made equal to that of the other parts of the object.

Figs. 8 and 9 will illustrate this.

[1] German Patent 76, 975, July 30, 1893.

If the cathode K is hung opposite to the anode A with no special precautions, then with the electrodes at too small a distance apart, great differences will occur in the values of the resistance elements, resulting in excess of current density around the point S. But if it is desired to coat over the whole spherical surface uniformly, then, as is shown in Fig. 9, a shield is placed before the object in such a manner that the apertures $oov_1$ are in the position shown. The course of the current lines will be thus deflected, until they will distribute themselves nearly uniformly over the whole cathode surface.

As long as the condition $\frac{I}{k\,g} = \text{const.}$ is fulfilled for all the elements of the cathode surface, the distribution of current-lines will be equal upon all parts of the cathode, producing a uniform deposit.

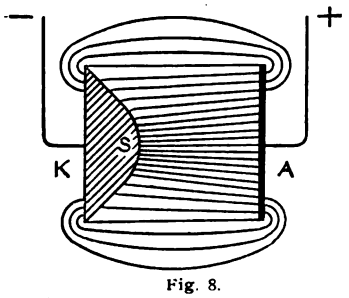



Fig. 8.

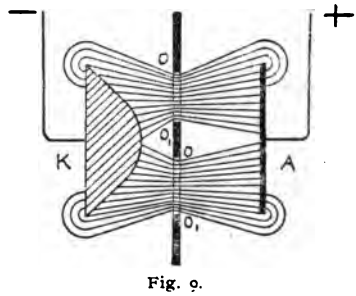



Fig. 9.

For sharp corners, the division is rather more difficult. The investigations of the author have shown an analogy between the path of the current-lines and the distribution of the magnetic lines of force and has shown that with larger electrode surfaces, above 1 square decimeter, and with electrode distances of more than 5 decimeters, the scattered current-lines will be more than 25 to 30 per cent. of the number of current-lines which would exist in a homogeneous field between two plane parallel electrodes. The amount of the scattering of the current-lines increases with the distance of the electrodes apart and decreases with the size of the electrode surfaces. The following expression will serve to approximately indicate the value of the coefficient of scattering,

$$\text{coef.} = \frac{1.25 \times l \times a}{s}$$

where $a$ is a factor depending on the conductivity and upon the electrolyte. Only a few very approximate values have so far been obtained[1] for this factor and it can only be said that in equally good conducting alkaline or cyanide solutions the coefficient of scattering of current-lines is greater than in acid solutions.

## DUMOULIN PROCESS.

The process of E. Dumoulin[2] is somewhat connected with a screen process. Dumoulin used his process for the production of objects with surfaces of rotation, basing it on the principle that inequalities in the surface of the precipitate are caused by unequal distribution of the molecules and especially by rough places upon the cathode. If an unevenness exists upon the cathode either before the current is started or afterwards, or as a result of the poor precipitation of the metal resulting from a bad preparation of the form or by a deposition of the slimy impurities from the electrolyte, Dumoulin insulates these points of unequal deposit until the surrounding parts have reached the same thickness.

The process is protected by the following patent claim.

Process for the manufacture of uniform electrolytic metallic deposits consisting in placing upon the cathode during the precipitation insulating material; producing this effect in a manner similar to the inking of type; reintroducing the surface into the bath wherein the insulating material itself is slowly removed, but not before the points coated have disappeared and become uniform with the whole surface of the cathode.

### *The Insulating Material.*

The materials used for insulation are tar, fat, vaseline, albumen and the like and the quantity of the insulating material used can be regulated by the workman in charge, and the growth of the surrounding deposit is thus regulated. It is clear that the current density will have a certain influence on the kind of insulating material used as well as the frequency with which the application is made.

The applications of this process are more extensively described later (see page 125).

[1] See Zeitschr. f. Elektrochemie 7, 895. Dr. W. Pfanhauser, "Ueber die Streuung der Stromlinien in Elektrolyten."

[2] German Patent 84, 834, April 9, 1895; English Patent 16, 360, August 31, 1895.

## METHOD OF THE FRENCH COPPER COMPANY.

The Societe des Cuivres de France[1] in 1894 obtained a patent based on the following principles:

If these conditions which are necessary for the obtaining of uniform deposits are not fulfilled, irregularities will necessarily appear, so that often with the most varied shaped anodes or even by arrangement of anode strips around the cathode, the irregularities cannot be entirely overcome.

The point referred to consists in surrounding the rotating cathode with anodes which are provided with projections or in general with equal "unevennesses." There is thus produced upon the rotating cathode a corresponding unevenness in the precipitate. The author believes the process to have a very limited application because slight projections on the anodes will soon be dissolved off and then will exert no further influence.

### Devices for Loosening of the Precipitates.

The precipitates are made upon particular forms, which, if of non-conducting material such as wax, gutta-percha, plaster of Paris, etc., must be made conducting by suitable surfaces of conducting material, such as graphite, finely divided silver, etc. Metallic forms are often used which are given an intermediate conducting coat if it is desired to remove the metallic precipitates upon them; the coating must be of such a nature that it does not combine with the metal, and yet does not hinder the conduction of the current. For such intermediate coatings the sulphides of the heavy metals may be used, or the metallic surfaces may be iodized or greased. W. Wood[2] proposed the graphitizing of non-conducting forms by the use of rubber dissolved in linseed oil; the further description of this is given in the special applications of galvanoplasty.

## PROCESS OF SUTHERLAND.

W. S. Sutherland[3] manufactured surface condensers by the precipitation of metal upon an easily fusible core, which was melted out at the completion of the precipitation.

[1] English Patent 23, 679, Dec. 5, 1894.
[2] English Patent Oct. 30, 1873.
[3] English Patent 8054, May 22, 1884.

## PROCESS OF REINFELD.

A. K. Reinfeld[1] had the idea to nickel plate the forms before using them, being convinced that traces of nickel dissolve in acid copper sulphate solutions, by which reaction a very small amount of copper is separated out which does not adhere to the nickel surface; so that by further electrolytic precipitation of copper it was possible to obtain a precipitate not adherent to the form and easily lifted off.

The loosening of the precipitate is easier if the nickel plated surface is treated with oxidizing agents or soap-like mixtures. In the latter case the surface of the form becomes extremely smooth because this mixture fills up any small unevennesses. The oxidation of the surface of the form can be produced by potassium chromate, or potassium manganate (the solution should be concentrated). The forms remain in this solution about 15 minutes, and are then washed and rubbed off.

### *Patent Claim.*

The process for manufacturing easily removable metallic precipitates electrolytically, consisting in providing a printing plate of any suitable form with a coating of nickel, or using plates alloyed with nickel, upon which the metallic precipitate is to be produced; treating these plates with chromium or manganese salts or soap-like mixtures for the purpose of making their surfaces perfectly smooth, whereby the easy removal of the metallic precipitate is rendered possible and subsequent polishing may be dispensed with.

## METHOD OF HOLL.

C. Holl[2] uses pure nickel as the form material for the removable precipitates. For greater cheapness he proposes to use also the following materials: cobalt, copper, steel, lead, cadmium, antimony, aluminium, tin; also ferro-silicon, ferro-chrome, etc. The materials used can also be supported upon glass in quite thin sheets and casings. Calcium chloride, also oxygen, either atmospheric or electrolytically produced, as well as other oxidizing sub-

[1] German Patent 50,656, Nov. 22, 1888.

[2] German Patent 74,564, Oct. 7, 1892. Supplementary to German Patent 50,656, Nov 22, 1888.

stances, render possible a preparation of the form in the manner desired. The main condition is always that the intermediate layer be insoluble in the electrolyte.

For instance, cuprous chloride, CuCl, can be used in copper baths for copper cathodes, silver cyanide for silver deposits in silver baths, or copper forms can be coated with a thin deposit of silver and the silver coating converted into a compound, with a non-metal, in order to facilitate the detaching of the subsequently precipitated copper.

*Patent Claims.*

1. The process of manufacturing easily removable metallic precipitates produced galvanically according to German Patent 50,890, by using pure nickel for the printing plate or form instead of a nickel coated or nickel alloyed plate.

2. In the use of the process of German Patent 50,890 and the process of the above Claim 1, the treating of the cathode either with various oxidizing agents such as chromium and manganese solutions or also with hydrogen peroxide, ferricyanide of potassium, chloride of lime, atmospheric oxygen, electrolytically produced oxygen or the precipitation of oxides insoluble in the electrolyte, or by insoluble conducting metallic cyanides, haloids, or sulphide compounds upon the surface of the cathode whereby the electrolytic deposition of the metal can be produced, different from the metal contained in the protecting intermediate coating, or the metallic surface of the form.

## ELMORE'S PROCESS.

The Elmore German and Austro-Hungarian Metal Company[1] patented in the year 1891 a method for the production of several consecutive cylindrical coatings upon a mandril. According to this process the metal is coated in place with a material which prevents adhesion of the subsequent deposit, such as fat, metallic sulphides and the like. When a precipitate has been formed on this the insulating process is repeated. It is thus possible to produce several layers on the same profile upon each other, and by cutting loose or otherwise separating from each other, sheets, ribbons, etc., are produced.[2]

[1] German Patent 64,420, July 7, 1891; English Patent 5,167, March 23, 1891, 14,624, (1890), 11,778, (1888); American Patent 484,704; French Patent 214,641.

[2] Compare also Burgess, Zeitschs. f. Electrochemie, 5, 334.

*Patent Claim.*

The process of producing several concentric cylindrical metallic precipitates consecutively on a mandril electrolytically, consisting in coating the surface of an already formed galvanic precipitate with a sulphide, fat or other material preventing the adhesion of a new precipitate and subsequently precipitating a further galvanic coating upon the one first formed.

## NUSSBAUM'S PROCESS.

A novel method of separating precipitates from the forms was proposed and patented in 1896 by A. Nussbaum.[1] The process itself will be further described at length and I limit myself here to saying that the easy and satisfactory removal of the precipitate from the particularly constructed model is obtained by introducing a fluid under pressure, which raises a valve-like part of the surface along with the precipitate upon it and so passes between the surface of the form and the precipitate.

The loosening can also be attained by depositing the metal at a free space upon the model upon a bolt so arranged that it can be unscrewed and removed, leaving a tube which serves as a pressure tube for introducing the fluid between the deposit and the mould.

## COLLAPSIBLE FORMS.

The Electro-Metallurgical Company, Limited,[2] uses collapsible forms from which the deposit is easily removed. The forms consist of thin metallic strips rolled in many windings upon each other. The loosening of the deposit is produced by drawing together the roll of strips by the assistance of the framework in the interior, which is gripped by a suitable tool; that is, the diameter of the successive rolls of ribbon are diminished and the precipitate becomes loose of itself, even when very long tubes are being produced.

Because of its elasticity, the form after being removed from the precipitate takes its original shape and size.

[1] German Patent 91,146, May 28, 1896. See also Zeitschrift des österreischen Ingenieur und Architekten-Vereins, 1899, 296. Engelhardt, "Ueber das Nussbaumsche Verfahren."

[2] German Patent 89,780, May 24, 1895; American Patent 592,802; English Patent 11,338, May 23, 1896.

*Patent Claim.*

The cathode for the reception of solid precipitates made elastic and spirally-formed so as to permit being rolled together and thus loosened from the precipitate and which in consequence of its elasticity retakes its original form.

## ELMORE'S PROCESS.

The Elmore German and Austro-Hungarian Metal Company[1] produces objects electrolytically, and uses as means of separating them from the mandril on which they are precipitated, the following process.

The thin metallic tubes which serve as mandrils for the precipitation are coated over with a material fusible at a low temperature and made smooth.

*Apparatus.*

The mandril *a*, in Fig. 10, is with its axle $a_1$ laid in a socket *b* of the frame *c*. The projecting part of the frame has a slit *d* in

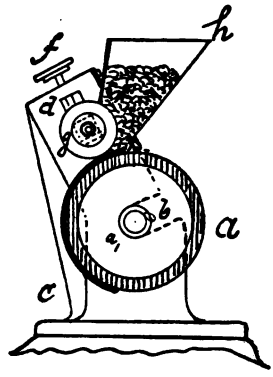



Fig. 10.

which are two boxes *e* adjustable by the spindle *f*. In the boxes rest the spindle of the roll *g* lying parallel to the mandril. This roll *g* can be so adjusted by the spindle *f* that it forms a wedge-shaped gutter with the mandril *a*, into which by means of the hopper-shaped vessel *h*, the material is fed which shall be used to coat over the mandril. The spindle $a_1$ of the mandril *a* is hol-

[1] German Patent 63,838, April 12, 1891; English Patent 7,932, May 22, 1900; American Patent 485,919; French Patent 212,385.

low and serves for the introduction and circulation of cold water; on the other hand, either hot air or steam is led through the roll g, the whole arrangement to keep the mandril cool and the roll warm. The coating material coming out of the funnel *h* is melted by the heat of the roll *g* and sets upon the cold mandril *a*. The thickness of the layer produced is regulated by the adjustment of the roll *g*. The coating may be either of an easily fusible metallic alloy or of some wax-like material. In the latter case, when non-conducting substances are brought upon the mandril, it is necessary to puncture the coating in numerous places through to the metallic surface of the mandril; or to effect this, to add to the coating material some salt easily soluble in water which can be washed out of the coating by immersion in water before placing in the electrolyte and thereby producing the desired porosity of the coating. The coating material can also be mixed with graphite.

When the electrolytically produced tube has been deposited upon the mandril the whole is warmed, as for instance, by introducing hot water into the interior of the mandril and so melting the coating upon it. The metal shell can then be easily removed from the mandril.

*Patent Claims.*

1. The process of facilitating the loosening of electrolytically produced deposits from a tubular mandril consisting in giving to the latter an easily fusible or smooth coating, soluble in a fluid, by the use of a rotating smoothing roll; in case the coating is non-conducting, providing it with numerous small holes, or mixing with it a conducting powder or a powder soluble in the galvanic bath, in order to produce a conducting path between the mandril and the conducting surface, such as graphite placed upon the non-conducting coating.

2. In the application of the process of Claim 1, in the case of using a coating soluble in a fluid the use of a tubular mandril provided with numerous perforations which are kept closed until the finishing of the perforated tube and which are afterwards used to facilitate the solution of the coating in a short time.

*The Best Material for Coatings.*

P. E. Preschlin[1] in connection with the Elmore German and Austro-Hungarian Metal Company patents as particularly advantageous, the filling of the tubular mandril with cold water in order to freeze immediately the coating placed upon it. The tube is first painted with asphalt varnish which produces a good adhesion of the coating. The latter consists of

| | |
|---|---|
| Paraffin wax | 75 parts |
| Pitch | 25 " |

This melts at 63° C. It is either poured upon the mandril or the cooled mandril is rotated while dipping into the melted material. When the coating has set, it is turned off smooth by the use of a strong jet of water. In this manner not only cylindrical tubes, but all types possessing a surface of revolution, and even helical surfaces can be made.

*Patent Claim.*

In the use of the process of patent 63,838 the production of an easily fusible coating upon a mandril by painting the latter with asphalt varnish and then giving it a coating of a mixture of wax and pitch with simultaneous cooling of its interior.

## COLLAPSIBLE MOULDS OF GERHARDI & CO.

German Patent 123,056, of December 13, 1900, of the firm of Gerhardi & Co., of Lüdenscheid,[2] is identical with the Steinweg process and recalls that of the Electro-Metallurgical Company, Limited. It is concerned with the manufacture of easily detachable galvanic precipitates and especially with the manufacture of nickel vessels.

*Objects of Pure Nickel.*

The previous processes for the separating of galvanic precipitates from their matrices are very little suited in many cases for nickel deposits; in some cases quite impracticable, especially when the precipitate is made upon a surface which is not quite even or upon a grooved or recessed matrix.

In depositing nickel the ordinarily used matrices of wax, rub-

[1] German Patent 72,195, April 6, 1893.

[2] English Patent 13,365, 1901, and German Patent, March 17, 1901

ber, gum arabic, and similar materials made superficially conducting, are impracticable since heavy deposits in a reasonable time can only be obtained in hot solutions in which the materials named above would become soft and lose their form.

The process of making the forms out of easily fusible metal and melting the latter out after the formation of the deposit has the great disadvantage of always forming an alloy with the first precipitated part of the deposit.

It is only possible in depositing nickel to use matrices of hard metal such as brass, copper or iron. Using such materials, only simple shaped flat objects or smooth hollow objects like cylindrical and conical objects can be made, or such as allow the removal of the core either by the contraction of the same or by the expanding of the precipitate by means of rolling, hammering, water pressure, etc.

The process is, on the other hand, not applicable for all other objects; that is, for the production of hollow vessels with constricted openings, recesses or off-sets or ornamental decorations.

*Process.*

The process to be described allows of the production of articles of any form whatever, and in particular, of hollow vessels of almost any desired form and with raised or recessed surfaces. The manner of working is characterized by the use of thin walled hollow metallic matrices made out of soft easily torn metals; for instance, of alloys of tin, zinc, or lead with antimony, bismuth, cadmium, arsenic, mercury, etc., the brittleness of which is increased when the temperature is made very low (using tin or tin-antimony alloys), or when the temperature is raised (as with tin, lead or bismuth alloys); and the side which does not receive the precipitate is provided with grooves or small linear recesses. The grooves which reach nearly through to the other surface divide the walls into strips or divisions. After the formation of the precipitate, the single strips are lifted and torn away by the aid of suitable tools. By properly dividing up the walls of the matrices in this manner, cores of almost any shape whatever are easily removed without changing the form of the precipitate.

The carrying out of the process may be varied in separate

cases. The material for the matrices is lead, tin, or an alloy, such as Britannia metal, as best suited to the purpose.

If the matrix is made of sheet metal, the sheet may be previously passed between rolls, one of which is smooth and the other provided with grooves and projections or the plate is laid upon a steel plate provided with corresponding projections, and the two passed together between two smooth rolls. With cast matrices, these grooves may be easily produced by providing the part of the mould which is back of the matrix with corresponding ribs or projections or the corrugations may be made by cutting by a suitable tool upon a lathe, a planing or a milling machine, or finally done by hand. In this case care must be taken that the tool does not cut too deeply so as not to damage the other side of the matrix.

The cuts or grooves can be made either before or after the formation of the precipitate. The direction of the grooves is preferably so ordered that the walls of the matrix are divided into single parallel strips which can easily be torn away. With objects of revolution it is often practicable to produce the grooves spirally so that the whole wall of the form can be rolled off in a single helicoidal strip. With complex matrices a further subdivision of the walls must sometimes be made.[1]

[1] See also Zeitschr. f. Elektrochemie, 8, 193.

# VIII. MANUFACTURE OF METALLIC POWDERS AND THE LIKE.

In order to produce directly metallic powders electrolytically there are two methods. It may be separated out cathodically from such solutions which do no furnish coherent precipitates, or it may be separated out of a normal metallic bath by precipitation upon a powdered cathode. The latter method must really be included in the art of galvanoplasty since it concerns a superficial coating of a conducting substance.

### PRINCIPLES.

If powder is to be separated directly from a solution of metallic salt, dilute solutions are used or such additions are made to the electrolyte as experience has shown will cause the separation of the metal in the form of a powder. Such additions may be, for instance, solutions of such metals which are more electropositive than the metal to be precipitated or a corresponding quantity of free acid.

### LEAD POWDER.

A fine crystalline powder of lead can be obtained from a solution of lead nitrate containing 50 grams of lead nitrate per liter if care is taken to keep the current density above one ampere per square decimeter of depositing surface. It is also important that the electrolyte be actively stirred, otherwise layers of solution rich in metal form at the bottom of the vessel from which lead is precipitated in another form.

### COPPER POWDER.

A strongly acid, quite dilute soltion of copper sulphate furnished copper in the form of a fine powder. The Elektrizitats-Aktiengesellschaft, formerly Schuckert & Company,[1] produce in this manner, and afterwards still further pulverize the powder according to the German Patent, No. 88,415, of August 15, 1896.

[1] German Patent 88,273, Aug. 24, 1894; Peters "Elektrometallurgie und Galvanoplastik," 1, 47 et seq. and Zeitschr. f. Elektrochemie, 3, 199.

*Principle.*

The primary condition is that a crystalline deposit always falls if compounds of higher valence are present in the electrolyte, which by reduction to lower valence, partly redissolve the metal precipitated.

*Example.*

Tin may be obtained as a fine powder if ferric chloride or ferric sulphate is added to the electrolyte along with small quantities of organic acids. The metal of these solutions added should not be precipitated by the current, which is easily effected by keeping the solutions correspondingly acid or alkaline according to the kind of metal in the solution added. Copper powder may be precipitated from cuprous chloride solutions if cupric chloride or ferric chloride is added continuously during the electrolysis.

In case that the metallic salt added is only raised to the higher state of oxidation during electrolysis, the current density at the anode is so regulated that as the anode is being dissolved some of the added salt is simultaneously somewhat oxidized or perduced.

*Process.*

The baths used are worked with an average tension of 0.8 volt and a current density of 220 amperes per square meter, the distance betwen the electrodes 10 centimeters. The solution is kept at room temperature and agitated by a stirring apparatus. When making a loosely crystalline mass of metallic copper, there are used anodes of cast copper 20 millimeters thick and cathodes of sheet copper 1 millimeter thick.

*Uses.*

According to the Austrian Schuckert Works, this product is capable of replacing bronze powder made in the ordinary way. Although the product is quantitatively satisfactory, it is, however, too heavy to compete with the ordinary bronzes. On this ground, no plant has been erected for the carrying out of the operation.

*Patent Claim.*

The process for the production of loosely coherent crystalline metallic masses suitable for the manufacture of metallic scales or

bronze powder, electrolytically, consisting in using as electrolyte solutions containing the metal to be precipitated and also other metals which are not to be precipitated and which are in the higher state of oxidation, and which are able to redissolve the precipitating metal forming its lower salts; the anode being soluble and of the same material as that being precipitated, and no diaphragm being used in the process.

## PROCESS OF THE SOCIETE CIVILE.

The Societe[1] civile d'etudes du Syndicat de l'acier Gerard subjects the metal to the action of the current while in the molten condition and in a thin freely falling column using high current densities and small tensions.

### *Applications.*

The process is suitable for the manufacture of metallic powders and also as an intermediate step in a process having for its object

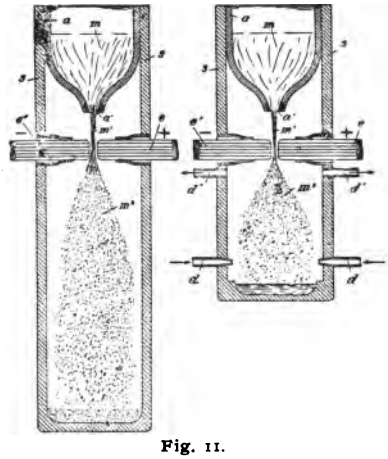


Fig. 11.

the subdivision of material without reference to its state of comminution or the final condition. The first use is illustrated by the production of lead powder for accumulator plates. The second method of application may be illustrated by the treatment of a finely divided stream of fluid iron with an excess of air for the production of steel.

The apparatus used is shown in Fig. 11.

[1] German Patent 89,062, Dec. 14, 1895; see also Zeitschrift f. Elektrochemie, 3, 227.

The melted metal is in the vessel *a*, in the upper part of the shaft *s* terminating below in the vertical middle plane of the shaft in a slit-like opening $a_1$. At some distance below the latter the electrodes *ee*, most suitably of carbon, project through the walls of the shaft, leaving between their parallel sides an opening corresponding to the above mentioned slit. The metal falls in a thin layer between the electrodes *ee*, is thereby finely divided by the current, its temperature is raised, and it falls as a rain $m_2$ in the lower part of the shaft where it collects as a powder or dust according to whether the particles fall a long distance, or the bottom of the shaft is artificially cooled, or the arrangement of a receiving fluid which may be placed in the bottom of the shaft, or a current of ascending gas which may be projected against it.

In case the transformation to powder or dust is only an intermediate step in the production of the material, in order to allow of the better action of a vaporized or gaseous reagent, for instance such as the steel manufacturing process mentioned above, the shaft may be provided at the proper distance below the electrodes with tuyeres for the introduction of the reagents; and higher up and closer to the electrodes, with openings *d* for the exit of the same or of the gaseous products resulting. (See Fig. 11, right hand side).

## PROCESS OF HOEPFNER.

L. Höpfner[1] obtains loose metallic masses in coherent flat plates. He first precipitates from the solution which may be of normal composition a pulverized or moss-like branching metallic mass by using high current density and for a period of 15 to 30 minutes, and then somewhat stiffens this by using a smaller current density for several hours and coats them with a coherent metallic plating.

### *Porous Copper.*

In order to make porous copper, the ordinary acid copper bath used in galvanoplasty can be employed. Starting with a high current density of same, 4 amperes per square decimeter, powdered copper is as is well-known obtained; this is followed by a

[1] German Patent 87,430, May 11, 1895; English Patent 17,671, Aug. 10, 1896; see also Zeitschrift f. Elektrochemie, 3, 130.

smaller current density, which is continued until the dark color of the powdered precipitate is changed into the well-known bright red color of electrolytic copper. If it is wished to work entirely with small current densities, a solution is used which contains less copper and more sulphuric acid.

*Porous Lead.*

Lead can be similarly obtained, but it is better to throw down the lead not in the state of powder, but in the form of leafy or moss-like crystals. The suitable current density for obtaining these leaves may vary between that which produces spongy lead and that which produces dense lead. This current is allowed to run for some time, then the current density is decreased somewhat in order to make the small leaves which are at first somewhat delicate more resistant. The regulating of the current density (from the stronger to the feebler) can be automatically adjusted by using at first a current density only a little greater than that necessary to deposit metallic powder or leafy lead; as soon as a certain quantity of metal has thus separated, the total cathode surface in contact with the electrolyte being increased, the new surface receives deposit with a lower current density, if the total current has been kept constant. For the production of the subsequent layers of metal successively higher current densities must be used. It is to be recommended to exert a small pressure upon the mass of leaf-like lead by means of a smooth surface, in order to reduce any large cavities and to obtain a uniform porous deposit. Not all lead solutions are equally well suited for the obtaining of such leaf-like lead. A solution of nitrate of lead gives for instance hard leaves which become brittle when pressed together, while a solution of lead oxide in caustic soda or caustic potash yields very soft and flexible leaves.

*Patent Claims.*

1. The process for the electrolytic production of metals in the state of a porous but coherent precipitate, characterized by the consecutive use of differing current densities by which a powdery or leaf-like or branching-mossy form of metal is first precipitated and afterwards dense metal.

2. In the process of Claim 1, the automatic regulation of the

current density by the use of an original current density only slightly above the limit of that which furnishes dense metal.

3. In the production of the leaf-like structure of metals as claimed in the process above described, the compressing of the electrolytically produced metallic leaves by a gentle mechanical pressure not sufficient to affect the porosity, used alternately with the application of the current.

4. In the process of Claims 1, 2 and 3, the use of a solution of lead oxide in caustic alkali as an electrolyte.

*Modification of the Process.*

Instead of changing the current density and using the same concentration of solution the former may be kept constant and the latter changed,[1] or to increase the effect both factors may be changed at once; for instance, a loose form of metal obtained by the use of a high current density and a low concentration of the electrolyte, and for producing dense metal high concentration with a suitable current density. Increasing the temperature acts upon the electrolyte in the same way as increasing the concentration. The best work is done in general by using for the deposition of loose metal the high current density at a low temperature and with a small concentration of the bath; and for dense metal higher temperatures, greater concentration and a suitable current density. Agitation of the electrolyte at the cathode or movement of the cathode itself acts similarly to increase of concentration or of temperature; agitation of the electrolyte permits of the deposition of dense metal.

Agitation acts therefore like concentration, particularly since it equalizes the dilution at the cathode because of the deposition of the metal from the solution. Its action is particularly to be noted when the electrolyte is agitated in order to reduce the polarization at the anode. Finally under quite similar conditions a change in the metallic deposit may be attained by putting the cathodes alternately into baths of qualitatively different composition; for instance, in the production of porous copper alternately in baths which are neutral or acidified by sulphuric acid, or for increasing these effects a change in the qualitative composition of

[1] German Patent 89,289, Jan. 1, 1896; Addition to German Patent, 87,430.

the bath may be coupled with changes in the current density, concentration, temperature or by decreasing agitation so that there is obtained first loose and then dense metal. To carry out regularly the alternations of the conditions named two different systems may be advanced, either the use of two separate cells and two separate electrolytes in which the cathodes are alternately plunged or working always in the same cell by changing the current density, temperature and agitation as well as also circulating through it fluids of differing concentrations and differing compositions.

It is recommended to combine both systems so that the loose deposit is treated in one cell first with a somewhat lower current density or slightly raised temperature until it becomes so strong that it will bear transporting to another cell where it will be still further strengthened. Since the surface of the cathode continually increases during the electrolytic process, a change from loose to dense metallic deposit can be allowed to proceed automatically if the conditions for obtaining the loose metal deposit are arranged at the beginning, as near as possible to the conditions necessary for the formation of dense metal. Now with a change of current strength, the change in temperature is particularly advantageous for the automatic regulation for the change in structure in the metallic deposit. It is to be recommended to particularly use a gentle pressure not injurious to the porosity of the metal. The process of patent 87,430 may be cheapened by the additional means proposed, namely of using agitation of the electrolyte and higher temperatures thereby producing also a very active depolarization of the anode. In fact, in for example, the separation of lead from not too dilute solutions of lead oxide in caustic alkalies, the anode remains permanently a metallic white, even with current densities of 200 amperes per square meter if high temperatures are used. Using high temperatures, the refining of the metal is much facilitated and cheapened since in consequence of the smaller bath tension the less electropositive metals do not go into solution. On the other hand, low temperatures are suited for the production of insoluble oxides and peroxides upon the anode. For example, extensive investigations down at a temperature of 9° C. showed that the anodes coat themselves over

with undissolved or insoluble oxides more quickly the lower the temperature.

*Patent Claims.*

Höpfner protects his process by the following comprehensive claims.

1. The method of carrying out the process of patent 87,430 for the electrolytic production of metals in the from of porous, yet coherent precipitates, characterized a) by alternate application of two solutions of different concentrations and such changes of the suitable current density in each case that at one concentration loose metal, at the other concentration, dense metal is precipitated; or b) by the alternate application of two different temperatures of the electrolyte and such changes of the corresponding current density that at one temperature loose and at the other temperature dense metal precipitates; or c) by the alternate application of rest and motion to the cathode or to the fluid at the cathode and such changes of the corresponding current density that in the one case loose metal and in the other case dense metal is obtained; or d) by the alternate application of two differently constituted baths and such changes of the current density that in the one bath the precipitated metal is loose and in the other is of a dense structure; or e) by the alternate application of two of the above described combinations included under the headings a) to d), and using suitable current densities so that with one combination loose metal and with the other combination dense metal is precipitated.

2. For the application of the process of Claim 1, a) to e) the separate and combined application of the two following systems; a) the alternate introduction of the cathode into separate cells in which the arrangements according to Claim 1, a) to e) are so adjusted that the cathode in the one cell is coated with loosely coherent metal and in the other with dense metal; b) the maintaining of the cathodes in the same cell in which, however, the current density, temperature, agitation or the presence of different electrolytes (the latter by circulation) are made to regularly alternate.

3. In the process of Claim 1, a) to e) the automatic regulation of the passage of the loose metal into the dense metal by the suit-

able utilization of the automatically increasing surface of the cathode and the diminution of the current density produced thereby.

4. In the process of Claim 1, a) to e) and 2, b): the use of arrangements for the automatic regulation of the temperature and the current strength.

5. In the process of Claims 1 to 4, the application of a gentle pressure not injurious to the porosity of the metallic precipitate, used alternately with the action of the current.

6. In the process of Claims 1 to 5, the application of a solution of lead oxide in a caustic alkali as an electrolyte.

7. In the electrolysis of dilute metallic compounds according to the processes described in Claim 1, a) to e), the use of impure metal as anodes for the purpose of refining it and the utilization of the oxides formed at the anode for the obtaining of by-products.

## PROCESS OF HUBER AND SACHS.

Huber and J. Sachs[1] produce metallic or metallized powder as a substitute for metallic and bronze colors, by precipitating the desired metal upon a core consisting of a conductor of the first class. The powdered cathode to be coated is agitated in the bottom of the electrolytic vessel in contact with a solid cathode conductor so that an intimate contact of the powder with the cathode conductor is assured with a continuously changing position of the particles. The anodes are parallel to the cathode plate and are separated from them by a clay diaphragm in order to avoid short circuits between the anode and the powdered metal in suspension.

### *Patent Claim.*

The process for the manufacture of metallic powder consisting in the electrolytic formation of a metallic coating upon a conducting powder which is kept in motion in a bath in such a manner as to be in contact with the cathode while contact with the anode is prevented by means of a diaphragm.

[1] German Patent 79,896, June 27, 1894; American Patent 521,991 and 521,992, June 26, 1894; American Patent 522,415, July 3, 1894.

# IX. MANUFACTURE OF METALLIC FOIL.

In order to produce metallic foil or thin sheets electrolytically, particularly prepared cathode sheets are usually hung opposite to anodes of the metal to be precipitated in a suitable electrolyte and left there until the desired thickness is reached.

### PROCESS OF REINFELD.

A. K. Reinfeld[1] pastes paper upon the thin copper sheet produced in the above manner and tears it away from its support. Reinfeld uses as cathode nickel-plated sheets which have been treated with oxidizing agents or soap-like materials in order to prevent the adhesion of the copper skin. In this manner prepared sheets of only 1 to 2 thousandths of a millimeter thickness are obtained.

#### *Operation.*

The well-nickeled and polished cathode is allowed to stand a quarter of an hour in a concentrated solution of potassium chromate or potassium manganate and is then rubbed off. The plates are covered on both sides with metal and the foil is obtained from the cathodes with a polish.

### PROCESS OF ENDRUWEIT.

C. Endruweit[2] makes copper and nickel foil by titrating the metal plate serving as a form with a concentrated solution of an alkaline sulphide, and after washing off with water dips it in dilute caustic soda solution. It is then again washed off and placed in the metal bath. Under some circumstances, it is recommended to have the plates connected as cathodes with a source of current when they are dipped into the caustic soda solution.

#### *Patent Claims.*

1. The process for the preparation of metallic plates upon which an insoluble skin of metal is to be precipitated in order to

[1] English Patent 3,222, Feb. 22, 1889.

[2] English Patent 2,724, Feb. 7, 1893; German Patent 82,664, Jan. 25, 1895. See also Jahrbuch, 2, 194.

manufacture metallic paper, consisting in treating the plate first with a solution of alkaline sulphide in water and immediately afterwards with a solution of caustic alkali.

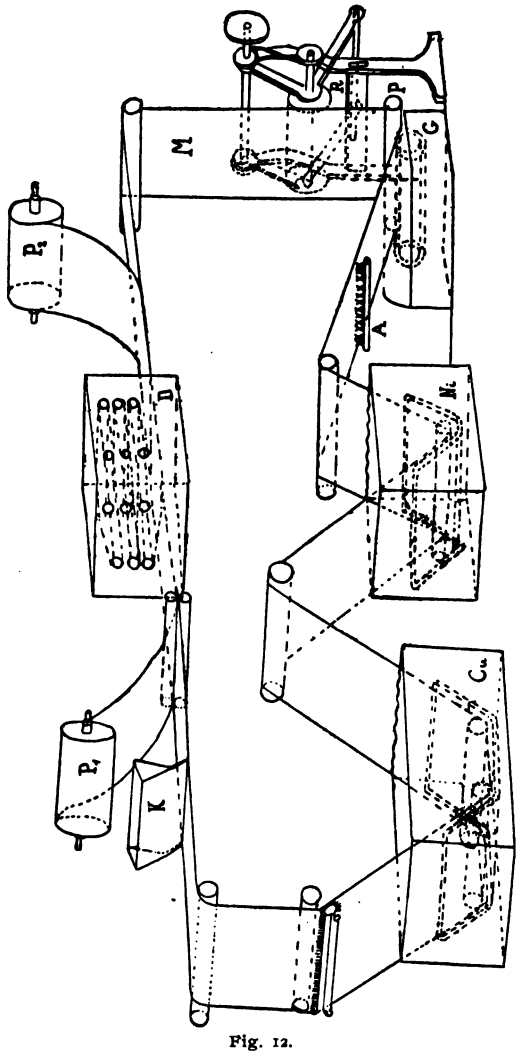



Fig. 12.

2. A special method of carrying out the process of Claim 1, especially suitable for plates upon which a skin of copper is to be

precipitated, consisting in connecting the plates as negative electrodes short-circuited to suitable anodes while being dipped in the caustic alkali solution.

*Improvements.*

Endruweit has arranged the process in such manner[1] as not to use a metallic plate as cathode but an endless metallic band (see Fig. 12).

The metallic band M passes in series through the roll R, the polishing roll P, passes then into the vessel G in which it is prepared by a 5 per cent. solution of alkaline sulphide. It then passes into the cleaning arrangement A, and thence into the nickeling bath Ni, where a thin film of nickel is deposited upon it, which as has already been explained, serves very well as an intermediate deposit. The copper bath Cu must self-evidently be of larger dimensions because the real precipitate is there given. Past the bath Cu there is a washing arrangement which frees the precipitate from electrolyte coming over from the last bath.

The backing paper which is rolled off from the spool $P_1$ by means of rollers is supplied continuously with the necessary paste from the holder K which distributes paste upon the precipitate. The pasted metallic band passes now to a steam drying apparatus D, and afterwards the finished metallic paper is stripped from the metallic band by a sharp instrument and rolled up upon $P_2$.

## ELMORE'S PROCESS.

Elmore's process of producing metallic sheets electrolytically by the production of a non-metallic intermediate coating has been already described on page 47 and is merely referred to here.

## DESSOLLE'S PROCESS.

L. E. Dessolle[2] produces lead metal and all kinds of useful objects which are to be obtained polished from the moulds, by saturating the surface of the metallic form with hydrogen. The form is first provided with a coating which is indifferent towards the electrolyte, and which is not quite removed by the hydrogen. Acids or alkalies may be used as electrolyte and anodes which are

[1] American Patent 676,357; see also Zeitschr. f. Elektrochemie, 8, 99.
[2] German Patent 98,468, Aug. 12, 1897. See Jahrbuch, 6, 333.

insoluble in the electrolyte. A voltage of 2.5 to 3 volts is used and the preparing operation lasts up to three hours.

*Patent Claim.*

The process for the preparation of cathodes for the immediate production of polished metallic sheets or other objects electrolytically, by placing upon the cathode a coating not soluble in the electrolytic bath, then saturating this coating in the electrolytic bath described with hydrogen and then polishing.

## PROCESS OF COWPER-COLES.

The process similar to that of Elmore (see page 45) was patented by Cowper-Coles in England in 1899, No. 16,210. The latter produces several concentric layers upon each other, and uses as an intermediate coating in order to facilitate detaching the deposit, an alcoholic solution of wax or a layer of metallic oxides or sulphides. The layer of oxide is obtained by heating in a mixture of air and steam, the sulphide layer by dipping into potassium sulphide. Cylindrical brass forms are used as cathodes which are rotated mechanically at a surface speed of 1,000 feet per minute. The precipitate comes down in this manner bright and coherent, although quite extraordinary current densities are used.

After several superimposed metallic sheets have been deposited, separated from each other by layers of wax or metallic sulphides, the whole is cut through parallel to the axis of the cylinder and the metallic sheets are separated from each other. The copper foil thus produced is used especially for making dynamo brushes.

## PROCESS OF LANDAUER & CO.

As an example of one of the processes which are used on a large scale for the manufacture of metallic paper, that of Landauer[1] may be described. In Landauer & Company's Galvanic Metal Paper Works in Vienna there is manufactured paper pasted to copper foil or nickel plated copper foil, as also other similar manufactures which are protected by a number of patents. Among the latter may be mentioned copper brushes for dynamos, coppered asbestos gaskets, flanged gaskets consisting of asbestos with a loose copper coating, etc.

[1] English Patent 15,573, July 15, 1898.

*Principle.*

earthen-ware 1 meter long, 50 centimeters wide and 70 centi-

Landauer precipitates copper, or first nickel, and afterwards copper, upon highly reflecting polished plates of brass or German silver, which have been first provided with the already described detachable intermediate layer; the metallic precipitate is dried, and then detached by itself or after being glued to paper.

*Baths Used.*

The baths used for precipitating the copper have the usual composition:

| | |
|---|---|
| Water | 1 liter |
| Crystallized copper sulphate | 200 grams |
| Concentrated sulphuric acid | 30 " |

For anodes there are used electrolytically deposited copper plates, 500x500 millimetres and 8-10 millimetres thick.

The precipitates must be prefectly smooth and free from protuberances. To this end, the electrolyte is continuously circulated and while circulating, passed through a filtration apparatus in the form of a small filter press so that it is always free from suspended solid impurities. The single baths are connected in series, the cathode plates of each bath in parallel. In each bath there are four anodes and three cathodes and between them moves a mechanical stirring apparatus provided with glass rods. The tension across the bath is only one volt with the electrodes about 10 centimeters apart, and a current density of about 10 amperes per square decimeter is used.

The dimensions of the lead lined wooden tanks are 700 millimeters long, 500 millimeters wide and 700 millimeters deep. If nickel metallic paper is to be produced, a plate prepared as before, is given a thin film of nickel precipitate in the following bath:

| | |
|---|---|
| Water | 1 litre |
| Nickel sulphate, $NiSO_4$ | 80 grams |
| Ammonium chloride, $NH_4Cl$ | 20 " |
| Boracic Acid, $H_3BO_3$ | 10 " |

The nickel deposit requires about one minute, a current density of about 0.5 ampere. The bath tension is 2.3 volts with the electrodes 10 centimetres apart. The tanks for the nickel baths are of

meters deep, and have supports and clamps for one cathode and two anodes. The anodes are of rolled and of cast nickel sheets mixed in equal numbers.

*Operation.*

The German silver plates, 400x500 millimeters are maintained with a highly lustrous polish in order that the metallic leaves may have a similar lustre and may be most easily detached. In the plant in question there are used for this process three polishing motors of 2½ H.P. each, driven by a single generator. For polishing there is used a composition of grease and lime. After polishing, the plates are freed from grease by lime water and pass then to the oxidizing or sulphiding baths. The time of this operation is about 5 minutes. After careful washing with water they are placed in the baths. They remain about 30 minutes in the copper baths, which are arranged in series of 30, there being two such series. Each series is run by a motor-generator furnishing 125 amperes at 35 volts. The operation is uninterrupted since for every plate taken out of the bath a new one is immediately inserted in order to avoid irregularity in the current-density relations. The coppered plates are given another washing and then placed in a drying room to remove the last traces of moisture, and then passed to pressing rolls where the paste is fed to them from a holder, the pasted surface covered with paper and then the plate and paper pass together through two pressure rolls. The pasted plate is again dried and the metallic paper then detached by loosening the edges with a knife-like instrument.

*Gaskets.*

If copper foil is to be made which is not to be pasted on paper, the copper precipitate is made somewhat heavier, the time of deposition being lengthened to 45 minutes, using the same current density as before. The flanged gaskets, that is, metallic copper gaskets with asbestos filling, are manufactured on a large scale in the works in question and have the following advantages. They are extraordinarily soft and possess in consequence of their tough elastic copper coating an extraordinary capability of making a tight joint, thus utilizing to the greatest extent the yielding qual-

ity of the asbestos. In this manner the asbestos filling is protected against the strong decomposing action of the steam, condenser or cooling water, etc., being protected by the seamless copper coating closed on the inside.

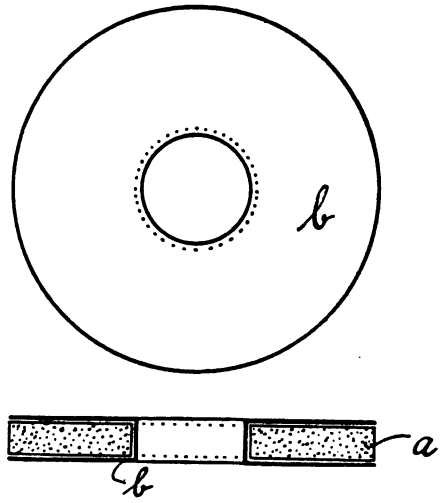



Fig. 13.

*a* is the asbestos filling, *b* the copper coating. In consequence of the continuous metallic surface of the ring, the burning fast of the gasket surfaces is prevented and the asbestos filling is therefore capable of being used over many times. The gaskets are manufactured by the quick electrolytic plating process devised by the author, the dynamo furnishing a thousand amperes at 6 volts, and driven by a separate electric motor, furnishing current for a 3,000 liter bath. The electrolyte is kept in oscillation by a compressor;[1] a tank has 9 cathodes and 10 anodes in parallel. The thickness of the precipitate is controlled by ammeters attached to each cathode conductor so that the bath is run independently of the size of the various electrodes. The thickness of the copper deposit is brought to 0.1 or 0.2 of a millimeter, the duration of the process, depending upon the current density used, is 15 hours for a current density of 6 amperes per square decimeter (see the corresponding table).

[1] See Pfanhauser "Elektroplatierung, Galvanoplastik und Metalpolierung," 4th Ed., 1900.

Brass rings are used as cathodes which are nickeled and provided with an intermediate stratum similar to that used in the plates for the manufacture of the metallic paper. The rings are as thick as the asbestos filling for which the copper coating is to be made; mostly 5 millimeters. The copper precipitates are loosened with a spatula-like instrument, the skill of the workman being an important factor in this work.

*Power Plant.*

As a source of power there is a 50 HP. steam engine furnishing regularly 35 HP., a dynamo attached to the machine gives current for the whole of the electrical power required. The plant has a total floor surface of some 600 square meters (6,600 square feet), and produces daily 3,000 sheets of metallic paper and 2,000 gasket rings and employs normally 60 hands. The copper used per year amounts to about 30 tons. The capital of the firm is $70,000.

*Costs and Profits.*

The firm of Landauer & Company have most kindly communicated to me their balance sheets of costs and profits, which I am permitted by them to reproduce here.

DAILY OPERATING EXPENSES.

| | | |
|---|---|---|
| 300 H.P.-hours at 1¼c | | $ 3 75 |
| 100 kilograms of electrolytic copper | | 30 00 |
| 60 workmen at 10c. per hour | | 60 00 |
| Superintendent at $1,000 per year | | 3 37 |
| 10% sinking fund on capital | | 23 75 |
| 5% interest on the capital | | 11 87 |
| 40% Government tax on wages | | 24 00 |
| Unforseen | | 5 75 |
| Total | | $162 50 |

DAILY OUTPUT.

| | | |
|---|---|---|
| 3,000 sheets of metallic paper at $90 per 1,000 | | $270 00 |
| 2,000 Gaskets at $300 per 1,000 | | 600 00 |
| | | $870 00 |
| 30% discount for the trade | $261 00 | |
| Producing cost | 162 50 | |
| | | $423 50 |
| Daily profits | | $446 50 |

The process of Landauer is carried on in Vienna by the Galvanic Metal Paper Works, formerly Landauer & Company; this firm also grants licenses for production in all other countries.

## LEAF SILVER AND LEAF GOLD.

The manufacture of leaf silver and leaf gold is quite easily accomplished by the principle of removable electrolytic coatings. From the many patents on this subject I select for mention those of Wood,[1] Perner,[2] and Brandt & Nawrocki.[3]

### PROCESS OF BRANDT & NAWROCKI.

This process uses copper plates as cathodes, and for avoiding the adherence of the precipitate there is used a thin intermediate layer of wax applied as a solution of wax in alcohol.

Where neutral or potassium cyanide solutions are customary as for gold, silver, nickel, brass, etc., a solution of rosin in benzole has been proposed. But for copper which is separated out of a strongly sulphuric acid solution, a coating of wax dissolved in alcohol of a strength of 1 in 50 is applied. The baths used are the usual galvanoplastic baths the composition of which can be found in special works on electro-plating.

*Time of Deposition.*

The time for depositing leaf gold and leaf silver is given in the following table:

| Metal. | Thickness of the metal leaves mm. | Current density in amperes per square decimeter. | | | |
|---|---|---|---|---|---|
| | | 0.05 | 0.1 | 0.2 | 0.3 |
| | | Time in hours and minutes. | | | |
| Silver | 0.0002 | 06½ | 03¾ | 01½ | 01 |
| | 0.0005 | 16 | 08 | 04 | 02½ |
| | 0.0010 | 32 | 16 | 08 | 05 |
| | 0.0020 | 1-04 | 32 | 16 | 10 |
| | 0.0050 | 2-36 | 1-18 | 39 | 26 |
| | 0.0100 | 5-12 | 2-36 | 1-18 | 52 |
| Gold | 0.0002 | 13 | 06½ | 03¼ | 02 |
| | 0.0005 | 32 | 16 | 08 | 05¼ |
| | 0.0010 | 1-04 | 32 | 16 | 10½ |
| | 0.0020 | 2-39 | 1-04 | 32 | 21 |
| | 0.0050 | 5-18 | 2-39 | 1-20 | 53 |
| | 0.0100 | 10-36 | 5-18 | 2-39 | 1-46 |

[1] English Patent 3,537, Oct. 30, 1873.
[2] English Patent 10,126, Aug. 7, 1886.
[3] German Patent 43,351, Sept. 25, 1887.

In the manufacture of metallic paper from gold and silver, the deposit of noble metal is usually strengthened by a galvanic deposit of baser metal in order to give a more durable and a more intimate connection of the metallic leaf with the paper. Copper or brass is mostly used in the case of gold leaf because according to experience the back ground works through the thin sheet of gold so that for instance copper gives to the sheet gold a reddish tint, to silver a greenish tint.

*Patent Claims.*

1. The process of manufacturing metallic paper (papier-mache or the like) consisting in first precipitating upon a suitable metallic plate an extremely thin metallic coating either chemically or galvanically, drying the same, furnishing the free surface of the same with a binding material, laying upon this moistened paper or paper pulp, and by a rolling process or pressure combining these so intimately that the sheet metal together with the paper can be detached from the support without being torn.

2. In the process of Claim 1, the variations: (a) that in place of a metallic skin two or more metallic films of different metals superimposed upon each other are produced upon the backing plate before the uniting of the metallic film or films with paper, paper pulp, papier-mache or the like: (b). Instead of placing the binding material first upon the metal-skin and then laying paper upon it, the placing of the paper, paper pulp, or papier-mache, or the like, already provided with a binding material upon the dry metallic film.

## PROCESS OF ENDRUWEIT.

The above process has several short-comings such as the small durability of the leaf metal upon the paper, and the necessity of polishing each time the cathode plates, such that the price of the metallic paper thus produced is about 25 cents per pack. C. Endruweit[1] claims to have invented a method by which the same amount of metallic paper can be made at a cost of 2½ cents.

*Patent Claims.*

1. The manner of conducting the process of Patent 43,351,

[1] German Patent 68,561, June 16, 1891; American Patent 510,013.

Claim 1, in which the insulating of the cathode plate from the metallic layer is done by means of a sulphide layer, consisting in moistening the plate with a 1 per cent. solution of alkaline polysulphides or acid hydrogen sulphide in methyl alcohol.

2. For the facilitating of the union of the metallic precipitate produced upon the cathode plate by Claim 1, with sheet paper the process of placing the cathode plate provided with a copper or nickel precipitate for a short time in a solution of zinc sulphate, being at the same time made the cathode of an electric current, and treating the precipitate thus produced with a solution of ammonium sulph-hydrate, mercaptan or allyl sulphide or of mixing of the just-named materials with the paste used.

Gilding or silvering is produced by rubbing the copper precipitate with a suitable cyanide solution containing gold or silver.

## PROCESS OF SCHROEDER.

E. Schröder[1] patents in Germany a process for the production of cathodes for the direct producing of polished metallic leaves electrolytically.

Schröder covers a highly polished and burnished metallic plate with a preliminary layer, a sort of enamel like material, which on being melted upon it produces a thin fluid glaze consisting of metallic oxides or similar mixtures. The lustrous polish of the backing metal sheets passes through this smooth coating, and the metallic precipitates upon these glazes are quite as dense and lustrous as if they had been produced upon the polished metallic plate itself. A single enameling suffices for several precipitations since the metallic sheets are very easily loosened and the plate is at once ready for a new coating.

In this way sheets of gold, silver and nickel are easily produced.

Schröder says that the enameling is injured neither in acid or alkaline, hot or cold solutions; but he assumes that the plates are always cathodically polarized, and that the conducting of the current is as explained by Streintz,[2] according to which the metallic oxides of the enamel being very finely subdivided as they are in such glazes, conduct the current to the metallic background.

[1] German Patent 123.658, April 6, 1900.
[2] Zeitschr. f. Elektrochemie, 7, 921.

## SHEET GOLD BY SWAN'S PROCESS.

J. W. Swan[1] produced sheet gold electrolytically upon polished thin copper plates using any usual gold plating bath; the metal being made as thick as is desired. The thin copper plates are then dissolved in ferric chloride solution or in nitric acid, leaving the gold as thin perfectly coherent films. In this way leaves have been made of less than 0.0001 millimeter in thickness, translucent to light.

## PRODUCTION OF PLANE SURFACES---RIEDERS' PROCESS.

Rieders[2] invented a process for the manufacture of smooth surfaces upon cast or rolled plates, galvanoplastically. The object of the process is to produce highly polished surfaces upon uneven surfaces such as are necessarily those of cast plates, and to

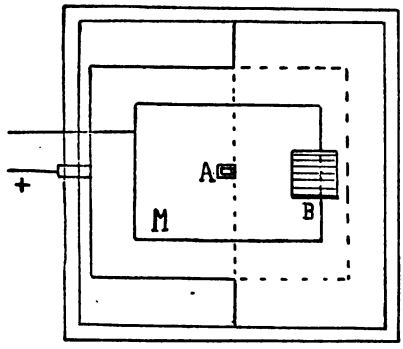



Fig. 14.

thus produce flat plates of a determined thickness. This process is intended to displace grinding or polishing work and to avoid the loss of metal connected with such processes. Rieders uses in his really ingenious process the following apparatus:

### *Apparatus.*

A polished glass plate G (Fig. 15) is fastened in the electrolyzing tank and polishes the metallic plate M to be smoothed. The spindle bent at K moves loosely in a bearing A of the metal plate. The plate is pressed against the glass table G by the movable heavy roller B, while the motion of the spindle causes the plate to

[1] L'Electricien XII. (1896), 173.
[2] German Patent 117,097, Dec. 15, 1899.

move eccentrically. The anode *a* is at the bottom of the vessel parallel to the plate M.

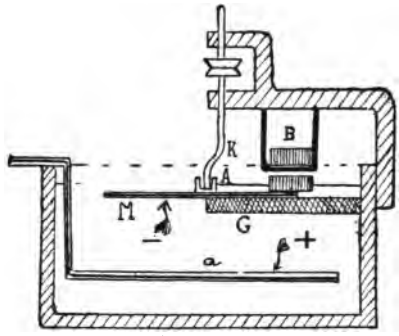



Fig. 15.

*Other Forms of the Apparatus.*

The appartus can also be constructed as shown in Fig. 16. In

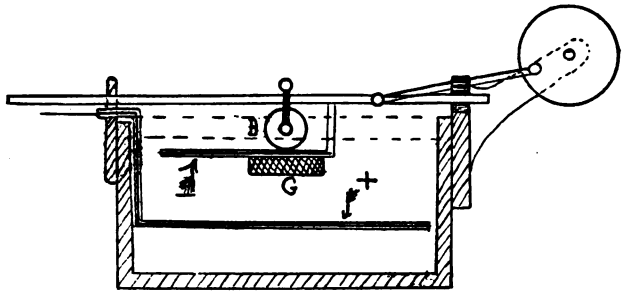



Fig. 16.

this the plate to be smoothed is moved backwards and forwards by an eccentric motion while the weighted roll B produces the desired pressure upon the glass plate G.

*Manner of Working.*

If a metallic plate which has cavities is coated in the ordinary way with a metallic precipitate, either the precipitate will deposit evenly and leave the cavities as they were, or by fast working the precipitate deposits preferably upon the projecting points accentuating the unevennesses. Rieders is of the opinion that the metallic precipitate forms more slowly on the projecting points

which come in contact with the glass plate since they are continuously ground off.

The action of the glass plate appears to the author, however, to be not completely understood.[1] But it must be assumed as a fact

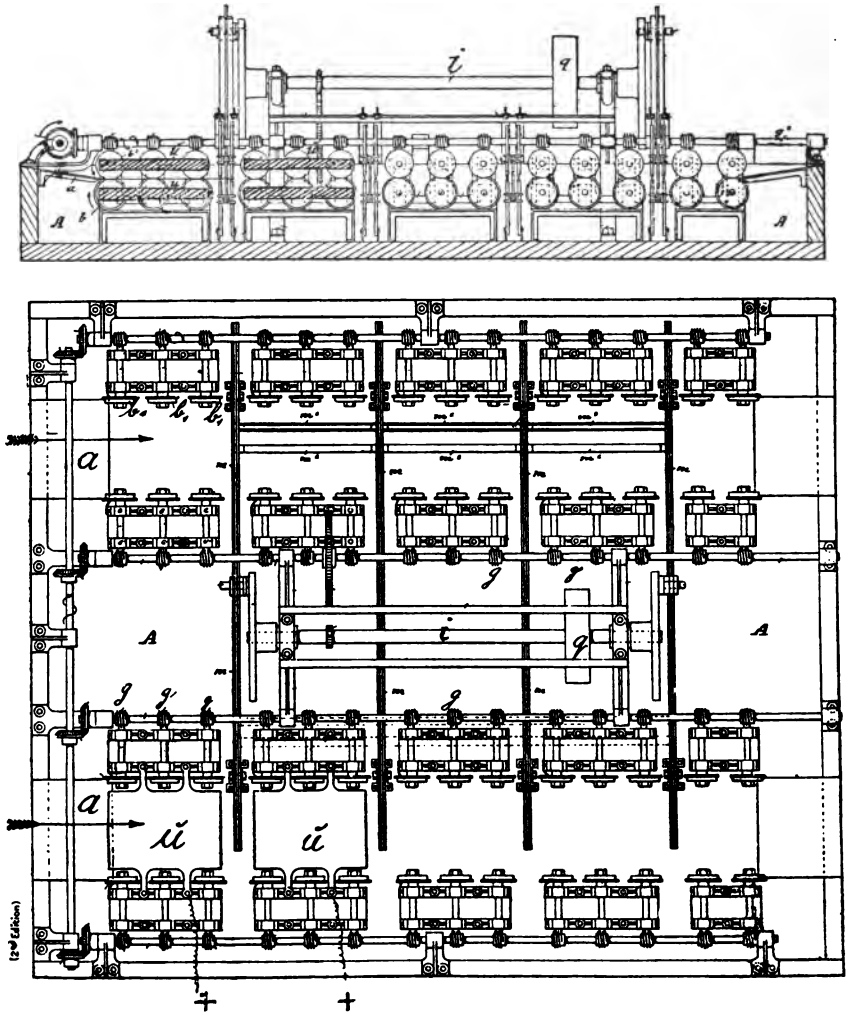


Fig. 17.

that perfectly even plates are produced by the apparatus, such as

[1] See also Zeitschr. f. Elektrochemie, 8, 88.

are used as plates in typographical work. There is a certain similarity between this process and that of Dumoulin, which will be described further on, yet Rieders says nothing of using a greasing or insulating material to protect the projecting parts of the plate.

## ELMORE'S PROCESS.

F. E. Elmore[1] has worked out mechanically a process for the production of sheets. He makes especially with his apparatus electrolytic metal sheets which are soft and which can be pressed to a high polish; such as for instance, copper, tin, silver, and the like.

### *Apparatus.*

The apparatus is shown in plan and elevation in Fig. 17. The plate *a* is moved by the rollers $b_1$ from left to right in the direction of the arrows, while the precipitate in smoothed by polishers. The apparatus is driven by the pulley *q*, the rollers by the worm gearing. The polishers are of agate or of the like and rest upon the cross rods *m*, which are rotated by the main shaft *i* by an eccentric. The anodes *u* lie above and below the plate operated upon. The prepared plates are taken from the movable table *a*, polished on both sides.

Continuous sheets and leaves can be made by modifying the apparatus so that an endless metallic ribbon is led over rollers, a suitable intermediate layer being first deposited upon it in any known manner.

[1] English Patent 9,214. July 15, 1886.

# X. PRODUCTION OF WIRE, ETC.

*Advantages of Electrolytic Copper Conductors.*

It has so far been practicable to produce wire of electrolytic copper only in such condition as to require a subsequent drawing, at least always when it is to be sold as commercial wire. Exceptions to this statement may be the quite thin leaves which are used as resistance ribbons. The high tensile strength possessed by electrolytically precipitated copper (see the work and investigations of Hübl) are possessed by no other electrolytic deposited metal, at the most excepting nickel, concerning which according to my knowledge nothing has been published as yet.

It is known that the conductivity of copper is extraordinarily influenced by impurities and it is the chemical purity of the copper produced by pure copper sulphate solutions which was primarily so greatly prized. In 1870 J. B. Elkington[1] patented a process by which electrolytically pure copper could be worked into wire without being melted.

### PROCESS OF ELKINGTON.

The method consisted in first precipitating thin copper plates electrolytically which were then cut into square strips. These were drawn out as usual, and when round in shape thickened up in the copper bath and again drawn.

### FOX'S PROCESS.

E. Fox[2] improved on the above patent in relation to the coppering of the wires, devising a suitable apparatus which had, however, no particular novelties.

### ACHESON'S PROCESS.

E. G. Acheson[3] patented a method of producing conducting wires which contain two separate insulated conductors. The metallic core of this double conductor is provided with a coating

[1] English Patent 2,525, Sept. 20, 1870.
[2] English Patent 3,455, Aug. 27, 1879.
[3] German Patent 38,914, June 2, 1886; English Patent 7,394, June 2, 1886.

of asphalt or the like and by drawing through a box holding graphite, is brushed over by mechanical means with a layer and made conducting. The wire is then coated electrolytically with a layer of copper, using at first a high current density and later a lower one until the desired thickness is obtained. The high current density must be used at first in order to copper over the graphite quickly while the subsequent smaller current density has the purpose of making the precipitate pliable. The bath tension is three volts at the beginning, and after the graphite has been coppered over this is reduced to one volt.

*Patent Claims.*

1. An electrolytic conductor consisting of a wire and insulating envelope of fibrous material and asphalt, a thin layer of electrolytically precipitated copper, a further coating of a metallic alloy and a protecting envelope.

2. The process of manufacturing the conductor described in Claim 1, consisting in coating over a layer of fibrous material and asphalt by brushing with graphite and so making it conducting, and passing it continuously first through a small bath using a high electromotive force wherein is deposited a proportionate hard crystalline layer of copper, and subsequently in a larger bath where, by a feebler current, a softer and more flexible copper precipitate is produced; and passing the wire then through a bath of an easily fusible metallic alloy.

## TAVERNIER'S PROCESS.

E. A. Tavernier[1] proposed to strengthen thin copper wires manufactured in the ordinary way by passing them through a trough by means of several rollers so that the path of the wire through the bath is as great as possible.

The construction of the apparatus is very simple. The wire runs inside the bath on insulated rollers either of porcelain or glass and outside the bath upon metallic rollers which drive the apparatus. Between the wires are the anodes, and the electrolyte is continuously moved by means of a suction pump.

[1] English Patent 1,680, Jan. 29, 1891.

## PROCESS OF SWAN.

J. W. Swan[1] uses the principle of precipitating copper continuously upon a cathode and then drawing it continuously through draw-plates in the process itself, thereby producing a smooth surface and the desired section.

### *Patent Claims.*

1. The process of manufacture of wire by electrolytic precipitation and drawing wherein the wire is simultaneously moved through an electrolytic bath and backwards and forwards through a drawing-plate.

2. The apparatus for the carrying out of the process of Claim 1 in which at both ends of the trough A provided with draw-plates $FF_1$ are placed drawing cones $DD_1$ and drums $EE_1$, upon which the wire is wound, and rotating these automatically by a source of power so that the wire is moved alternately backwards and forwards through the bath and the drawingplates.

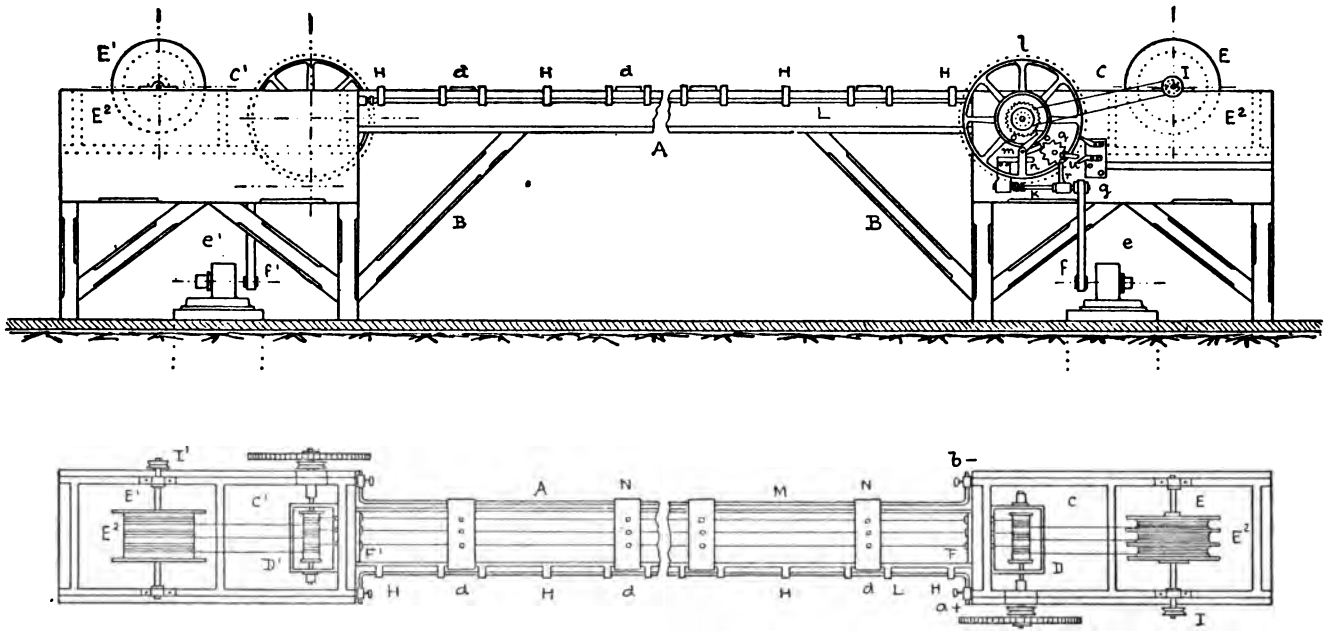
### *Apparatus.*

Swan uses for his apparatus that shown in Fig. 18. In a long narrow trough A is an electrolyte of normal composition. The two ends of the trough are closed by the plates $FF_1$ provided with the drawing holes. Outside of the plates $FF_1$ are spaces $CC_1$, in which are two drawing drums $DD_1$ which keep the wire stretched. From here the wire passes upon a much larger drum $EE_1$ in a washing box where the wires are washed. The driving of the drum $EE_1$ is by means of the pulley $JJ_1$. The wires are connected as cathodes with a source of current by the contacts M and the current is lead in by the brushes N. The conductors N are passed through glass tubes and insulated from the copper anodes ii by bushings of non-conducting material. There are several such conductors in a bath.

### *Placing of the Wires in the Apparatus.*

The wires are so placed in the apparatus that at one end of the trough A, for instance, the end adjacent the drum $D_1$, the wire is passed through the hole in the draw-plate $F_1$ and then fastened

[1] German Patent 63,030, Oct. 9, 1891; English Patent 19,586, Dec. 1, 1890; see also Lum. elektr. E. Andreoli, (1892), 45, 66.


E'
C'
H
d
H
d
H
H
l
C
I
E
E²
E²
A
L
B
B
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f'
e
f
K
q
q
I'
E'
C'
E²
D'
F'
A
N
M
N
b-
C
E
E²
D
F
H
d
H
d
H
d
L
H
a+
I

Fig. 18.

upon the drum $D_1$. The latter is then turned until a length of wire equal to the length of the trough is wound up. The fastened end is then loosened and the drum again revolved, the loose end then being fastened to the drum $E_1$. This is continued until the wire is completely drawn through and wound up upon the drum whereupon the other end is passed through the drawing plate F at the other end of the trough and fastened to the drum D. Each of these wires which serves as a carrier for the precipitate should be at least four times the length of the trough A.

*Operation.*

For making copper or silver wires the bath is worked at a temperature of 20° C. The apparatus serves also for the manufacture of nickel wires, but must be altered to work with warmer solutions. For copper a tension of 1 volt is used and the bath contains not more than 3 per cent. of free sulphuric acid, otherwise the copper suffers in regard to tensile strength. The table in the appendix gives exact figures concerning the current strength used. It is self-evident that the current strength to be used is regulated according to the number of meter lengths of wire being electrolytically produced as well as according to the diameter of the same which regulates the surface.

The rate of drawing is regulated according to the current density used and the dimensions of the drawing holes. With a normal current density of 1 to 1½ amperes per square decimeter the velocity of drawing would not be more than 1 meter per minute, in order to bring the surface of the wire as often as possible in contact with the edges of the drawing holes and so to produce a compression and smoothing of the deposited copper.

Two electric motors $ee_1$ are best adapted for driving the apparatus, each furnishing 1 horse-power. These two motors rotate the drums $DD_1$ alternately so that the wire, becoming always thicker as the deposit increases, is drawn forwards and backwards through the holes of the draw-plate $FF_1$ and wound up on the drums $EE_1$. While the wire is drawn by the drums D or $D_1$ from the trough, fresh wire is simultaneously wound off the other drum $D_1$ or D and is carried forward into the trough by the winding drums and there receives a fresh coating. When this

newly coated and thickened wire comes to the other end of the trough it is drawn through the draw-plate there and wound up at that end; then the direction is changed and the operation is so conducted until, because of the deposit of metal from the bath, the desired length of wire has been produced.

The two driving drums D and $D_1$ could be automatically operated by an arrangement to be described later, or in case electric motors are used for driving, a suitably connected switch could be operated by a contact, best placed on the end of the wire so as to throw the electric motors $e$ and $e_1$ alternately into and out of action. It may be seen in Figs. 18 and 19 that each of the two

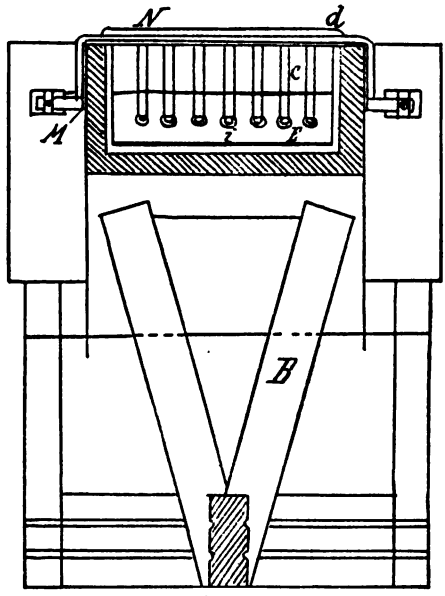



Fig. 19.

drums D and $D_1$ is driven by its own electric motor by the pulleys $f$ $g$ and worm gear drive $k$ $l$. If it is desired the source of power can be directly connected with the screw shaft $h$ by a coupling. A pawl $m$ fastened to the gear wheel is held against the ratchet wheel $o$ fastened upon the axle of the drum D, by the pressure of a spring $n$. The spur wheel $q$ fastened to the gear wheel $l$ on one of its spokes is turned around one tooth at each revolution of

the gear wheel *l* by striking against a fixed projection of the latch *r*. The latter prevents a reversal of the wheel *q*. At each revolution the wheel *q* lifts by a small rod the latch *m* out of the toothed wheel *o*, so that the drum can turn freely in the reversed direction by a pull of the wire from the drum at the other end of the trough.

Simultaneously with the lift of the latch or immediately thereafter the current-making contact *m* fastened on the wheel *q* touches another contact and makes electrical connection between this and a current closing piece upon the wheel *l*, whereby the circuit is closed by the switch throwing the formerly operating motor out of the circuit and the other electric motor into the circuit so that the direction of motion of the wire is reversed. In this way the wire is mechanically drawn backwards and forwards until the desired length has been produced and the wire is of the desired thickness.

According to the calculations of the author a trough 10 meters long should produce in 10 hours the following quantities, if it is assumed that 30 draw-holes are used so that there is exposed to the electrolytic deposition 300 meters of wire at one time.

| Diameter of wire in mm. | Weight produced in 10 hours Kg, | Current used for whole apparatus in amperes.[1] | Surface per running meter in square decimeters. | Area of wire in square millimeters. | Weight per meter in grams. |
|---|---|---|---|---|---|
| 1 | 14.2 | 120 | 0.31 | 0.79 | 6.99 |
| 2 | 28.4 | 240 | 0.62 | 3.14 | 27.96 |
| 3 | 42.6 | 360 | 0.93 | 7.07 | 62.95 |
| 4 | 56.8 | 480 | 1.24 | 12.57 | 111.90 |
| 5 | 70 0 | 600 | 1.55 | 19.64 | 174.80 |

It is to be seen from this compilation that the smaller wires are made under unfavorable conditions, because the cost of operating, interest and sinking fund would be increased when making them.

*Cost of Plant.*

For a wire-drawing establishment to produce 100 kilograms of copper wire daily of various sizes between 1 and 5 millimeters in diameter the cost of plant would be as follows:

[1] Current density used 1.3 amperes per square decimeter.

| | |
|---|---|
| 3,500 square yards of ground | $ 1,625.00 |
| Buildings with 2,000 square yards of shedding | 875.00 |
| Boiler, 70 square yards of heating surface with masonry and chimney | 3,000.00 |
| 60 H.P. steam engine, including foundation, etc | 2,500.00 |
| Main generator, 35 Kw., with switchboard | 1,250.00 |
| 35 Swan apparatus, including electric motors | 12,500.00 |
| Switchboard, measuring instruments, conductors, etc | 1,125.00 |
| Erection, packing, freight | 1,500.00 |
| Putting in operation | 625.00 |
| Total cost of plant | $25,000.00 |

*Operating Costs.*

For a plant of the above capacity the operating costs would be:

| | |
|---|---|
| Coal: 3.3 lbs. per H.P.-hour, per year of 300 days of 24 hours each = 650 tons at $3.75 | $ 2,437.50 |
| 72 tons of blister copper at $237.50 | 17,100.00 |
| Wages of the foremen | 1,500.00 |
| Wages of one clerk | 500.00 |
| Wages of one engineer | 375.00 |
| Wages of two firemen | 550.00 |
| Wages of ten workmen | 2,500.00 |
| Dynamo brushes, grease and polishing material | 750.00 |
| 5% interest on capital | 1,250.00 |
| 10% sinking fund | 2,500.00 |
| Light, heating, etc | 250.00 |
| Total yearly operating cost | $29,712.50 |

*Profits.*

Assuming the price of copper wire at 41.5c. per kilogram (18.64c. per pound) and that the above plant produces yearly 72,000 kilograms = 159,400 pounds, the profits would stand as follows:

| | |
|---|---|
| 72,000 kilograms of wire at 42.5c. per kilogram (18.64c. per pound) | $29,880.00 |
| Value of 0.4% silver content of the blister copper at $19.00 per kilogram | 5,500.00 |
| Value of 0.003% gold content at $700 per kilogram | 1,500.00 |
| Total | $36,880.00 |
| Operating cost | 29,712.50 |
| Yearly profits | $ 7,167.50 |

Corresponding to a dividend of 28 per cent.

*Applications.*

The fundamental condition for the profitability of this attractive process is the obtaining of rich blister copper since it can be easily calculated that if electrolytic copper were used which is free from the noble metals, the process would no longer be profitable. Whenever the price of pure electrolytic copper would be over 28.75c. per kilogram the process would also be unprofitable.

**PROCESS OF SANDERS.**

R. D. Sanders[1] obtained a patent together with a number of supplementary patents, the claims of which are as follows:

The production of wire or ribbon electrolytically by means of a conical, prismatic or otherwise shaped cathode, the working surface of which is spirally grooved with the adjacent grooves insulated from each other.

A cathode for the production of wire or the like electrolytically using a cathode with non-conducting insulated spaces, similar to that of patent 71,838, characterized by so forming the non-conducting spaces or the conducting cathode spaces that the desired sectional shape of the wire or ribbon can be produced, and that the metal can be deposited on either, sideways or in a direction perpendicular to the cathode surface.

A method of carrying out the process of the above patent for the production of wire and like objects, characterized by placing in the grooves of the mandril used as cathode a wire which facilitates the detaching of the electrolytic deposit.

The production of wire electrolytically using a starting wire as a depositing surface, which wire is wound upon a spindle so as to be detachable, and instead of being sunk into deep grooves is wound upon the surface of the cylinder or in such shallow depressions that the wire projects above the cylindrical surface of the spindle so that rubbing contacts would lie continuously on the starting wire or on the deposited metal.

*Principle of the Process.*

From these patent claims it can be seen that Sanders works

[1] See also Zeitschrift f. Elektrochemie, 1, 428.
German Patent 71,838, Feb. 16, 1892; English Patent 7,960, May 8, 1891.
German Patent 73 824. May 18, 1893: English Patent 12,382. July 4, 1892.
German Patent 78,361, March 22, 1894; English Patent 13,931, July 18, 1893.
German Patent 104,185. Aug. 26, 1898.

upon the principle of a revolving roller using a conducting roller wound spirally upon a mandril, deposits metal electrolytically upon it, and thus produces a metallic deposit like a spiral spring. Sanders thereby saves much space and simplifies considerably the apparatus of Swan. The wire is loosened from the backing and drawn through the ordinary apparatus whereby the seams of the spiral of the flattened surfaces which are against the mandril are caused to disappear.

*First Apparatus.*

Sanders' first apparatus was constructed as follows: A roller was made of wooden disks clamped together and placed in a holder and covered over with a non-conducting or a conducting material. In this coating a spiral groove was cut or in the case of the non-conducting coating was then covered with a conducting material either in the grooves or upon the ridges. If the coating was of metal the grooves were filled with wax or a similar non-conducting material. The wax having hardened the whole roller is turned so that the ridges of the metallic surfaces of the spiral grooving are visible. If a conducting material is to be used the roller with its coating is turned smooth and is given a metallic coating such as tinfoil. The coating having become hard a spiral groove is cut in which leaves upon the grooves a strip of the metallic coating in the form of a spiral line. The roller is as large as can conveniently be used which allows easier winding off of the finished wire. The coating is best made of asphalt or the like.

*Use of Finishing Tools.*

While the roller is being rotated burnishing tools can be applied to it. As soon as the tools arrive at one end of the spiral the direction of rotation of the roller is reversed. The burnishing tools are carried in frames which move in guides fastened to the sides of the vessel. The motion of the burnishing tools is given by the spiral winding of the roller itself.

*Second Form of Apparatus.*

In the first apparatus the metal showed a tendency to grow upon the non-conducting parts, so that the patent 73,824 was

directed towards the use of angular cathodes. In this manner precipitates of nearly circular cross-section are obtained.

Fig 20 shows a cathode carrier with recessed construction. Be-

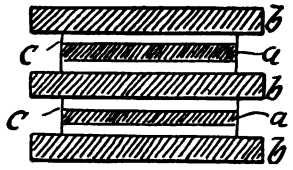



Fig. 20.

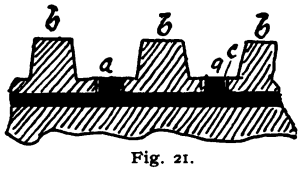



Fig. 21.

tween the strips *b* are layers *c* of non-conducting material in which are embedded metallic plates *a* upon which the precipitate is formed. Fig. 21 shows a cathode carrier upon which the metal can be deposited spirally in great lengths. If wished, this cathode carrier can also be made of a cylindrical form. In all cases the visible surfaces of the metal strips upon which the deposit takes place are not so wide as the bottom of the grooves, so that the deposited metal can spread sideways as it increases in amount until the desired cross-section or the desired amount has been reached. In a similar manner it is evident that a large variety of cross-sectional forms can be produced, as for instance, in Fig. 22, in which a spiral groove is formed upon a cylindrical metallic

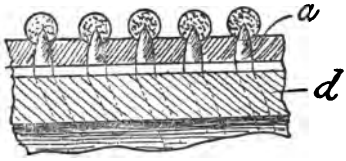



Fig. 22.

mandril *d*. This groove is filled with non-conducting material, and then the whole cylinder turned down, leaving upon the outer surface a thin visible metallic line *a*. The metal precipitated upon the latter takes then an almost circular form. In taking off the wire it is self-evident that the surface under the deposit will appear as a long groove which can be, however, pressed together afterwards. For producing longer wires the cathode surface is constructed in the manner shown in Fig. 23. The metal band is rolled up spirally and the intermediate spaces filled with non-conducting material. The flat sides are turned off or cut down to

the edges of the metallic band so as to leave visible on each side a thin screw-like metallic surface *a*.

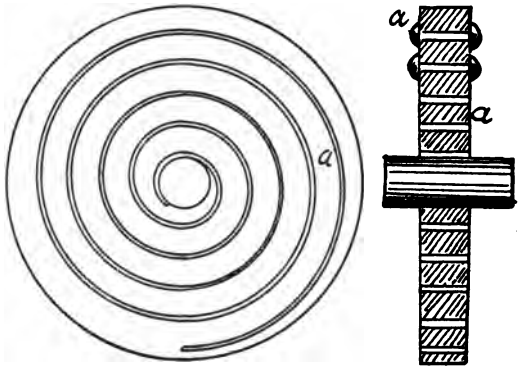



Fig. 23.

If the deposited metal is to be rubbed during the deposition an arrangement, as shown in Fig. 24, is used in which the cathode

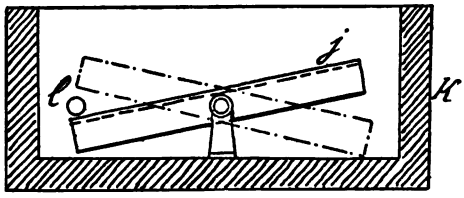



Fig. 24.

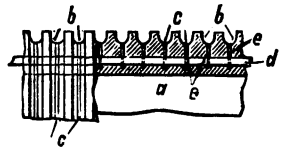



Fig. 25.

carrier *j* is pivoted in a vessel *k* and a roller or a rubbing pad *l* lies loosely upon the upper surface of the cathode. This roller must have sufficient weight to smooth out the deposited metal by its motion.

### *Loosening of the Wire.*

The separating of the backing wire from the precipitate is facilitated by laying in the grooves of the mandril or roller a fine wire which forms the true depositing surface. During the electrolysis the groove is filled up with the deposited metal and at the end the metallic precipitate can be rolled off with or without the original wire. It is required to make a smaller groove in which the wire is laid so that it cannot be surrounded by the precipitated

metal. The mandril consists of any suitable material such as porcelain or glass.

Upon the mandril is a spiral groove *b* in which the fine wire *c*

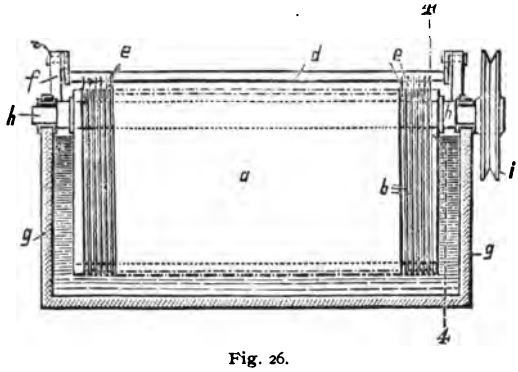



Fig. 26.

is laid. The ridges or wires *e* form a conductor between the fine wire *c* and the larger coductor *d*, their free ends rest upon the upper surface of the wire *c* and the other end fastened into holes in the conductor *d* which latter is held by a bracket *f* fastened to the holder *g*. If the deposited metal is such that it does not adhere to the original wire, such as is the case with lead it can be removed without disturbing the original wires.

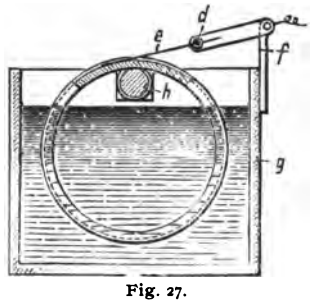



Fig. 27.

In those cases where the conductor is arranged outside of the mandril or kernel the latter is hung upon a rotating shaft, and in order to avoid deposition of metal upon the rods *e* is so hung that a part of its circumference extends above the level of the fluid. This manner of supporting the mandril can also be used when the material of the mandril encloses the conductor. The rotating

shaft *h* is turned in any suitable manner by the pulley *i*, (see Fig. 27), and preferably above the level of the liquid in the trough *g*. By this arrangement when the shaft *h* is rotated the mandril *a* is by friction slowly rotated in the fluid. Metal is deposited upon the wires *c* and the pencils *e* carry the current.

### *Operation.*

In operation several shafts are run by a common shaft the rotating speed being best about 1 meter per minute. The power required per roller varies according to the number of burnishing tools, the size of the trommel and the surface velocity, and is between 0.2 and 0.5 HP. The power necessary for electrolysis is not included in this. The bath tension varies between 0.25 and 0.7 volt. In order to obtain as great a tensile strength and the best conductivity of the wire it is recommended to use pure electrolytic copper or blister copper containing at least 98 per cent. copper. The burnishing tools are best made of agate of proper shape to give to the wire the desired form in which it is to be sold. For round wires agate tools are used, which are cut with a semicircular groove in them.

### *Cost of Plant.*

In order to compare this process with that of Swan the cost of the plant will be calculated likewise for a production of 100 kilograms of copper wire per day; the wire being assumed as 5 millimeters in diameter, which can then be drawn to any desired size.

COST OF PLANT.

| | |
|---|---|
| Ground, about 10,000 square feet | $ 250.00 |
| Building for electrolytic and drawing plant, with office and dwelling for the superintendent | 2,500.00 |
| Boiler of 300 square feet heating surface, including masonery and foundation | 1,375.00 |
| Steam engine, 30 H.P | 1,750.00 |
| 30 Sanders' apparatus, 3 feet long and 2 feet diameter including burnishing tools | 6,375.00 |
| 7,500 gallons of electrolyte | 875.00 |
| 10 Kw. dynamo | 625.00 |
| Switchboard with equipment and conductors | 1,000.00 |

| | |
|---|---|
| Drawing apparatus and reels | 1,200.00 |
| Belts and pulleys | 1,125.00 |
| Washing tanks | 200.00 |
| Erection, packing, freight | 500.00 |
| Starting expenses | 925.00 |
| Total | $18,750.00 |

OPERATING COST.

The following values can be assumed:

| | |
|---|---|
| Coal 3.3 pounds per H.P.-hour at $3.75 per ton = per year | $ 1,250.00 |
| 72 tons of 98 per cent. blister copper at $237.50 per ton | 17,100.00 |
| Superintendent | 1,500.00 |
| Clerk | 500.00 |
| One engineer | 375.00 |
| Two firemen | 550.00 |
| Fifteen workmen | 3,750.00 |
| Dynamo brushes, lubricating oil, etc | 750.00 |
| Five per cent. interest on capital | 937.50 |
| Ten per cent. sinking fund on the capital | 1,875.00 |
| Lighting, heating, etc | 250.00 |
| Total, about | $28,837.50 |

PROFITS.

Assume the same selling price of the wire, that is 41.5c. per kilogram (18.87c. per pound).

| | |
|---|---|
| 72 tons of wire | $29,880.00 |
| Value of 0.4 per cent. silver in blister copper at $19.00 per kilogram | 5,500.00 |
| Value of 0.003 per cent. gold in blister copper at $700 per kilogram | 1,500.00 |
| | $36,880.00 |
| Operating cost | 28,837.50 |
| Yearly profits about | $ 8,042.50 |

Corresponding to a yearly dividend of almost 43 per cent.

It is therefore seen that the Sanders process possesses a better outlook than the Swan, starting with the same conditions. I must remark that the price of the Sanders apparatus has been found by approximate calculation, and there may be some further variation in the value from that given.

## PROCESS OF FORSYTH AND FLETCHER.

A process similar in principle to that of Sanders for producing metallic ribbons and rods was patented by Forsyth and Fletcher. The apparatus used by them is constructed as follows:[1]

### *Apparatus.*

The wrought iron cylinder F closed at both ends is covered at the ends with an insulating layer B, on the sides with a metallic covering of easily worked metal G. (Figs. 28-30). A spiral

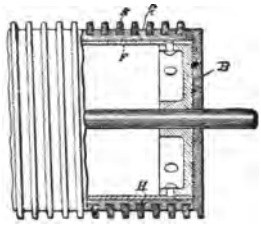


Fig. 28.

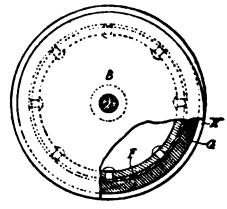


Fig. 29.

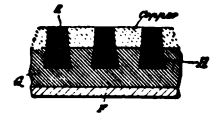


Fig. 30.

groove of trapezoidal cross-section is cut in the metallic sheath with the larger base of the trapezium beneath and in these grooves strips of insulating material K are placed, which may be of rubber.

This roller is then hung as a cathode in an electrolytic metallic vessel and rotated, when the metal deposits between the rubber strips K, so that when the electrolysis is stopped it may be wound off as a metallic band, or if the electrolysis is carried on longer may be obtained as wire or rod having a cross-section determined by the form of the rubber strips between which it is deposited.

## PROCESS OF COWPER-COLES.

To complete the list of these processes I mention that of Cowper-Coles, by which sheet metal or metal strips or wire may be produced in any desired lengths.

### *Apparatus.*

Cowper-Coles[2] deposits the metal upon an endless copper band which is drawn so slowly through the electrolyzing vessel that

[1] American Patent 570,125, Oct. 27, 1896; see also Zeitschr. f. Elektrochemie, **3**, 346.

[2] English Patent 2,998, 1895; Zeitschrift f. Elektrochemie, **2**, 648.

the precipitate on leaving the bath is of the desired thickness; it

Fig. 32.

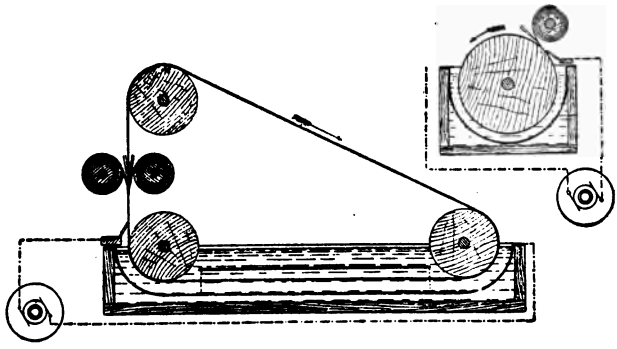


Fig. 31.

is then separated from the band outside of the bath and rolled up on a reel. (See Figs. 31 and 32).

# XI. MANUFACTURE OF BODIES OF LARGE SIZE.

The largest application of electrolytic metallic depositing processes is the manufacture of tubes of all varieties; but before turning to this use we will describe those processes dealing with the manufacture of large bodies such as large vessels, parabolic mirrors, etc.

## PROCESS OF J. KLEIN.

A completely new method of producing bodies having the shape of surfaces of revolution of most varying kinds was patented by J. Klein.[1] This investigator likewise compresses the metal as it is being deposited by causing a rotating cathode to roll against a corresponding shaped straight or grooved support.

### *Patent Claims.*

1. The process for the compressing and forming of electrolytic precipitates characterized by using roller-like cathodes of any desired number and profile and rolling them upon corresponding straight or grooved supports in an electrolyte bath until the end of the operation.

2. The carrying out of the process described in Claim 1 by the use of an apparatus consisting of one or more frames in which (according to the number of the bodies to be produced at once) either one, two or more rotating mandrils are rolled upon a vertical, inclined or horizontal or curved support, backwards and forwards, until the precipitate upon the mandril is of the desired thickness.

3. The apparatus of the kind described in Claim 2 in which the mandril is hollow and open at one or both ends and the metallic deposit upon which is compressed by smoothing irons while the deposit upon the inner surface of the mandril is compressed by one or more rollers carried upon a rotating frame.

[1] German Patent 79,764, March 31, 1892; English Patent 563, Jan. 9, 1895; see also Zeitschrift f. Elektrochemie, 1, 161; Dr. G. Langbein.

4. An apparatus of the kind described in Claim 2 so altered that it or at least the frame is arranged as a turning rack within whose sweep the mandrils are rotated and so radially movable, while the form has the shape of a fixed hollow cylinder the inner or outer circumference of which is rolled by the movement of the turning rack.

5. The apparatus of the kind described in Claim 2 in which the frame is arranged as a rotating disc which in its motion rolls the mandrils, arranged radially about its turning axis, upon a horizontal plate.

As far as concerns the process used by Klein it can be judged from the same how the process is carried out since the different constructions of the mandrils as well as the whole apparatus are minutely described.

*Manufacture of the Mandrils.*

The mandrils upon which the metal precipitate is deposited consist either of metal or wood and can be hollow or solid. See figures 33 to 36.

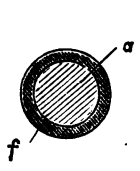


Fig. 33.

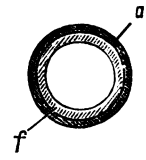


Fig. 34.

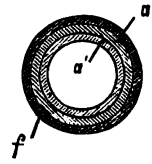


Fig. 35.

Fig. 36.

Fig. 33 shows a solid mandril, Fig. 34 a hollow one, Fig. 35, one which is stiffened by an included tube, while in Fig. 36 the mandril is stiffened inside by one or more cross ribs.

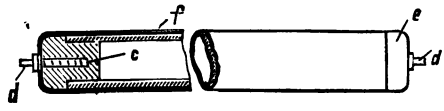


Fig. 37.

The adjustment of such hollow mandrils is made clear in Fig. 37. The mandril is closed by the plug *e*, which has a small screw plug *b* and a conducting contact *e*, the latter having the form of a cap. The hollow mandril is usually filled with sand or lead shot. The stiffening webs of the mandril are then filled up by the appli-

cation of gypsum, glue, clay, or the like, or at once coated with an easily fusible and polishable material, such as wax, lead, paraffine, etc. The form is then rolled upon the properly prepared former giving it the form of rotation desired. Instead of rolling the mandril with its plastic coating it may also be turned down to the shape desired; the surface of the roller is then made conducting in the proper way if it is of non-conducting material. The arrangement shown in Fig. 38 is particularly designed for produc-

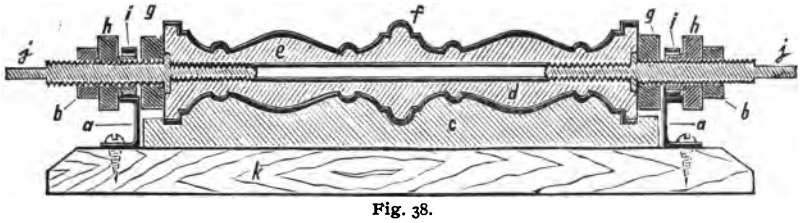



Fig. 38.

ing hollow rotated bodies. It consists of two exterior parallel guides *a* screwed down to a base *k*. Between these guides is the form *c* having the profile of the desired article. The hollow body is carried by the tube *d*, forming the center of the mandril. The ends of the spindle *j* are furnished with screws in order to hold the article fast in position. On both sides of the spindle are rollers *g* and guides *h* so that the guides *a* lie between them. The mandril is fastened in position on the spindle by the nuts *b*.

The tube *d* is then coated with clay and rolled backwards and forwards upon the base *c*, previously rubbed with oil, and rolled until the desired form corresponding to the base has been obtained. The guides *h* roll freely upon the track *a*. The mandril is now burned and then dipped into a mixture of resins or wax, after which it is again rolled upon the former in which operation the rings *ii* placed upon the sliding guides regulate the thickness of the coating. In putting on the wax coating the burned form is wetted with water to prevent the adhesion of the wax. The mandril so coated is then made conducting either with graphite or with an easily fusible alloy if the mandril has not been coated with wax.

For the forming, various arrangements can be used and Figs. 39 and 40 show several types. This forming is to be distinguished

from the forming of the mass of clay on the forming table since the forming arrangements to be described serve to compress and polish the precipitate during the electrolytic process. Figures 39 and 40 show quite simple apparatus.

*Simple Form of Apparatus.*

In the electrolyzing bath A the forming plate *h* is placed on the supports *g*, being of hard material like glass or procelain not attacked by the bath. If several mandrils are to be simultaneously worked they can if they have the same profile be rolled upon the

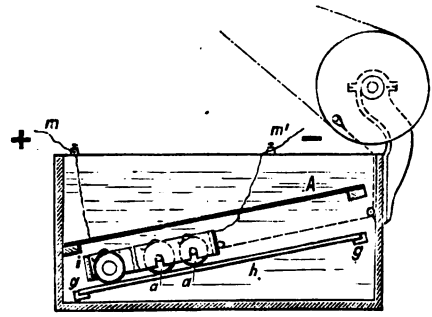



Fig. 39.

same forming plate if they are put together in the frame *i*, being so placed in the frame that they can be easily taken out one at a time. The conducting of the current to the mandrils is by the wire $m_1$ by means of the brush L, fastened to the frame and the already mentioned contact pieces on the ends of the mandrils. The anode is above the forming mandrils and parallel to their direction of motion.

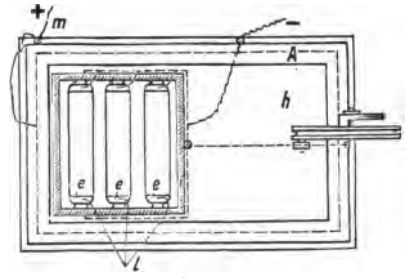



Fig. 40.

As soon as the current is put on metal begins to deposit on the

forming shape, and the frame is moved backwards and forwards upon the forming plate by an eccentric. Figs. 41 and 42 show a

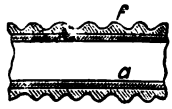



Fig. 41.

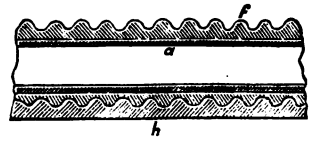



Fig. 42.

cross-section of the forming plate.

Fig. 43 shows a form of apparatus which is a multiple of that shown in Figs. 39 and 40.

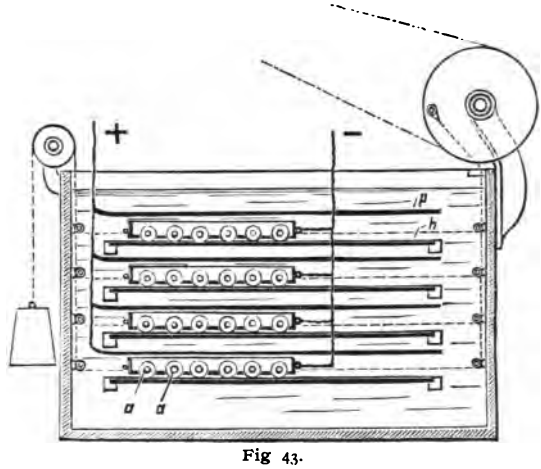



Fig 43.

The longitudinal and cross-sections of a forming vessel are shown in Figs. 44 and 45. In this several forming cylinders can be simultaneously worked over in a vertical direction in which case the frame is carried by the rollers $r^1$ and the mandrils are pressed against the forming plate by the rollers $r^2$. The frames can also be pressed against the forming plate by adjustable wedges or in any similar manner. The anode plates are bent to correspond approximately with the profile of the cylindrical forms and take part in the motion.

*Circular Apparatus.*

Another shape of the apparatus is that having a trough-shaped arrangement of the forming plate. The best form is that of a

hollow cylindrical arrangement of the plates because in that case both the forming plate and the anode can be given the desired profile by a turning operation. Such a form of apparatus is

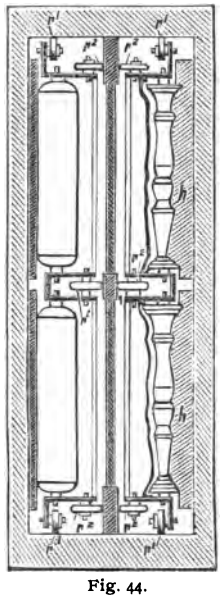


Fig. 44.

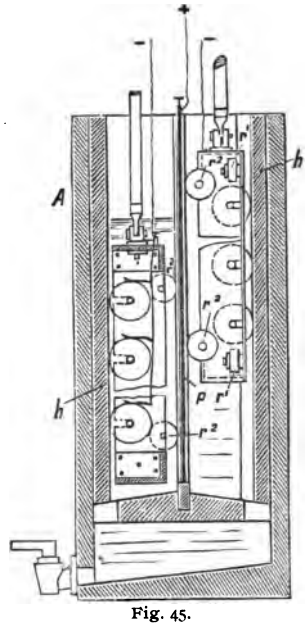



Fig. 45.

shown in Fig. 46, in which *b* is the forming plate in the shape of a cylinder and fastened to the outer case of a holder *c*; *d* is the turn-

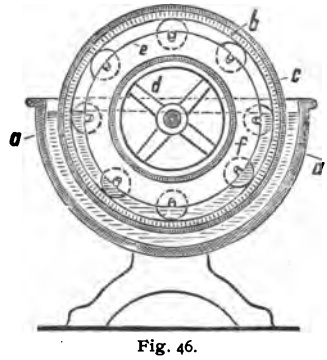



Fig. 46.

ing frame carrying the cylindrical anode *f* and two discs *e* on the axle of the forming cylinder lie in slits opening out-

wardly. If the turning frame *d* is moved alternately in one or the other direction whereby the cylindrical formers are pressed, either simply by centrifugal force or by any other method the precipitate

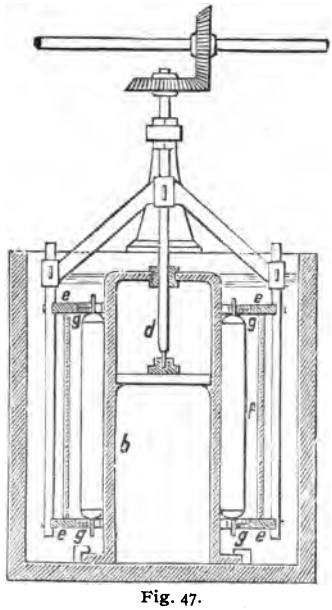



Fig. 47.

is smoothed out in the same manner as if the forming plates were plane. The apparatus of Fig. 47 is constructed similarly with the

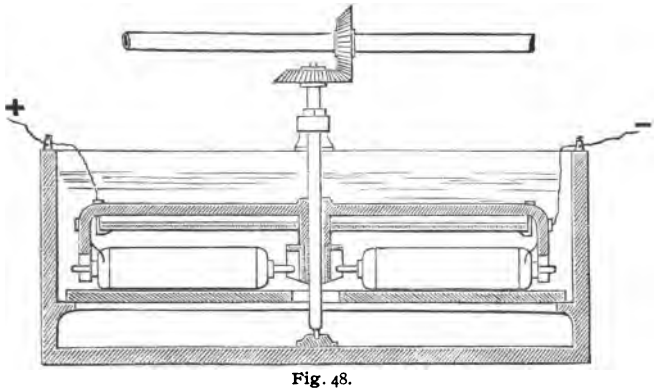



Fig. 48.

slight additions that the cylindrical forming plates are placed vertical and the cylinders travelling over them are placed inside.

A radial arrangement of the cylindrical rollers upon a concentrically moulded forming disk is shown in Fig. 48. In Fig. 49 the

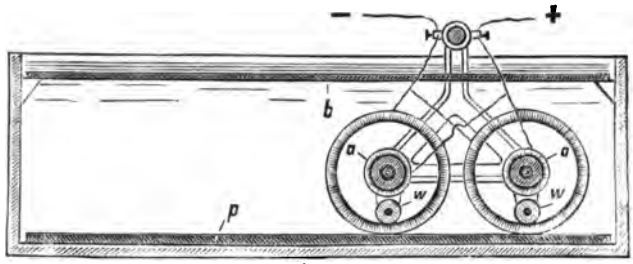



Fig. 49.

forming of the precipitate upon the inner and outer surfaces of the two hollow forming cylinders is shown, in which internal rollers *w* and an external forming plate *p* are used. In this case two anodes must be used, an inner and an outer, marked *a* and *b*.

### *Advantages and Applications.*

The advantages of the Klein process are evident without further discussion. It requires a minimum of space and a small amount of electrolyte. It is able to produce any described article having for its outlines a surface of revolution, which is not the case if the cylindrical formers are used without the aid of the smoothing or forming plates.

The process is very suitable for many purposes and experiments have been made to produce by it corrugated boiler tubes. Since the most various profiles can be obtained in this way the Klein process has decided advantages over the many methods for the production of tubes.

## NUSSBAUM'S PROCESS.

The process of A. Nussbaum,[1] consists in the manufacture of copper vessels and the like using a fluid under pressure between the deposit and the mould. This is done in the simplest manner by causing the fluid under pressure to pass through a valve-like arrangement at the inner surface of the deposit and to raise up the latter and pass between it and the mould; the electrolytic deposit is extended at one side of the mould into a nipple by means of a

[1] German Patent 91,146, May 28, 1896; see also Engelhardt: III Internationaler Congr. f. angew. Chemie: Chem. Zeitg, **22**, 649, (1898).

bolt or protuberance in the mould which on being screwed out leaves a tube which serves as a means of introducing the fluid under pressure between the deposit and the mould.

The apparatus for the practical carrying out of the process is shown in the accompanying figures.

Figures 50-54 show the mould with the valve *v* which is then coated with the deposit *u*. Fluid under pressure is then pumped

Fig. 50.

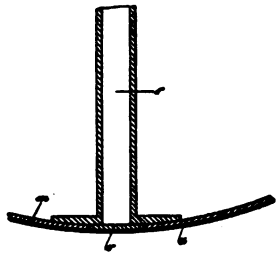


Fig. 52.

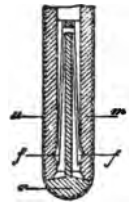


Fig. 51.

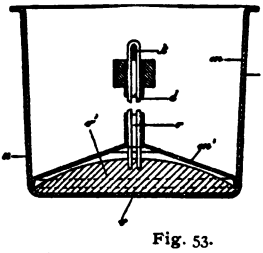


Fig. 53.

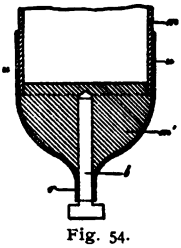


Fig. 54.

into the center of the hollow mould or best by means of the pressure tube *n*, where it lifts the valve *v* at the surface of the mould. The pumping in of the fluid must proceed slowly at first in order to give it time to insinuate itself between the surface of the mould and the precipitate and so to enlarge the effective pressure surfaces; otherwise the precipitate may rupture at the valve. The complete separation of the precipitate is indicated by a slight crackling; with larger objects several cracklings may be heard corresponding to the loosening of the different parts. After a few further strokes of the pump the precipitate separates from the mould.

*The Valve.*

The valve $v$ must close tightly in order to prevent the entrance of the fluid under pressure into the mould and to perfectly complete the unbroken surface of the mould. The best shape is a slightly conical valve.

Small valves keep tight by simple greasing, larger ones must be held down by a suitable spring $f$, or by a bent wire $d$ with a projecting wedge $k$ fastened to an enlargement $v^1$ of the valve. The spring $f$ under the influence of pressure of the fluid slides easily out of its seat and thereby leaves the valve open. The bent wire $d$ must be freed by the loosening of the wedges $k$ before pumping in the pressure fluid in order to render possible the pressing out of the valve $v$.

Vessel moulds having a convex bottom may be provided with smaller valves, but these require rather high pressures. Vessels with flat bottoms must, however, have valves almost the size of the bottom and be strong enough to withstand the pressure; otherwise the flat bottoms will bulge out or even burst. In the manufacture of open tubes it is recommended to make them with a hemispherical auxiliary bottom and valve because the convex depositing surfaces stand the pressure better which is necessary for the removal of the tube.

The valves are easily loosened from the precipitate, if necessary, they are given several blows with a wooden hammer. If a tube with an open end is to be made the precipitate at this end is cut off, the valve inside pushed out. In making small tubes, the tube serving as the mould can be also the pressure tube, but must in this case have a greater thickness of walls than the precipitate. For larger articles a special pressure tube is used in which case the tubes acting as the moulds can be made correspondingly slimmer because they do not have to withstand inner pressure. The separation and loosening of the precipitate is easier in this case because the mould is somewhat compressed by the pressure and the pressure fluid can more easily find its way along the precipitate.

*The Pressure Tube.*

The pressure tube is either fastened permanently to the mould

by means of flanges or is pressed firmly against the flat bottom of the vessel and its free end arranged for connection with the pressure pump. It is better to place them in the axis of the mould at the bottom of the same. In the case of long articles in which the precipitate cannot be axially removed from the mould, several pressure tubes can be placed at suitable distances from each other. By pumping the pressure fluid into the several pressure tubes the precipitate can be successively removed.

*Raising of the Precipitate.*

The loosening of the precipitate is possible, Fig. 54, in the case of open vessels without using a valve. The metallic tube is closed at its open end by means of an auxiliary piece into which a bolt passes. When a sufficiently thick deposit has been formed on the pressure tube the auxiliary piece and the bolt, of which the head of the latter has been protected from receiving a precipitate by means of a coating is then turned out and the tubular nipple-form of the precipitate is then fastened to the pressure pump, for instance, by tapping it with a screw-thread. The separating of the precipitate results as when using the valve arrangement.

*Patent Claims.*

1. The process for the loosening of electrolytic precipitates by pumping in a fluid under pressure between the precipitate and the metallic surface.

2. A method of carrying out the process of Claim 1, characterized by the use of a pressure fluid which raises a valve-like movably arranged part of the surface together with the precipitate thereupon and thereby passing between the precipitate and the mould; in connection wherewith for the introduction of the pressure fluid the use of either a hollow formed mould itself (*m.* Fig. 50) or a particular pressure tube (*r,* Fig. 50 and 53) fastened against the body of the mould.

3. A second method of carrying out the process of Claim 1, in which the electrolytic precipitate is prolonged at an open place of the mould by means of a bolt (*b,* Fig. 54), for the purpose of connecting to the nipple formed pressure tube after the withdrawal of the bolt.

As is shown in the following calculation of profits[1] the Nussbaum process should soon replace the old coppersmiths' work.

COST OF PLANT.

For a plant with a daily output of 900 kilograms, or yearly 300 tons of copper vessels and using 100 HP.

| | |
|---|---|
| (a) Dynamo | $ 3,000.00 |
| Measuring instruments and switchboard | 212.50 |
| Main conductors | 87.50 |
| Unforseen | 125.00 |
| Erection | 337.50 |
| (b) 200 baths with stirring apparatus, without solutions and anodes, at $106.25 | 21,250.00 |
| (c) Pumps, lathes and various tools | 2,512.50 |
| (d) 3,000 moulds at $4.25 | 12,750.00 |
| (e) 81 tons of anode copper at $300 per ton | 24 300.00 |
| (f) Electrolyte ($CuSo_4 + H_2SO_4$) | 7,500.00 |
| (g) Water-power plant with turbines at $127.50 per H.P. | 12,750.00 |
| (h) Buildings, 1,700 square yards shedding | 14,375.00 |
| 200 square yards brick building | 2,550.00 |
| 5,000 square yards ground | 2,125.00 |
| (i) Purchase of patents | 25,000.00 |
| (k) Working capital | 12,500.00 |
| Total | $141,375.00 |

OPERATING COST (YEARLY).

| | | |
|---|---|---|
| 1. | Wages: 50 workmen at $191.25 | $ 9,562.50 |
| | 1 foreman | 500.00 |
| | 2 engineers at $375.00 | 750.00 |
| 2. | 300 tons of electrolytic copper at $300 per ton | 90,000.00 |
| | 3 per cent. waste of anode material | 2,700.00 |
| 3. | Lubricating material, etc | 450.00 |
| 4. | Sinking Fund. | |
| | 10 % of the electrical equipment ($3,875) | 387.50 |
| | 15 " " bath equipment ($21,250) | 3,187.50 |
| | 10 " " machinery equipment ($2,512.50) | 251.25 |
| | 15 " " cost of moulds ($12,750) | 1,912.50 |
| | 5 " " cost of electrolyte ($7,500) | 375.00 |
| | 5 " " cost of the water-power plant ($12,750) | 637.50 |
| | 4 " " building cost ($19,050) | 762.00 |
| | 8 " " cost of the patents | 2,000.00 |

[1] The following data I owe to Chief Engineer Engelhardt.

| | | | |
|---|---|---|---|
| 5. | Interest: | | |
| | 5 % of the working capital (12,500) ..... | | 625.00 |
| | 2 " " cost of the anode copper (24,300). | | 486.00 |
| 6. | General expenses: | | |
| | Superintendent ..... | $ 1,250.00 | |
| | Two clerks..... ..... | 1,500.00 | |
| | Insurance..... | 250.00 | |
| | Taxes ..... | 6,250.00 | |
| | Diverse expenses..... | 3,300.00 | |
| | | | $ 12,550.00 |
| | Total ..... | | $127,136.75 |
| | Rounded to..... | | 127,500.00 |

PROFITS.

| | |
|---|---|
| Assuming the value of the 300 tons of ware at $575.00 per ton..... | $172,500.00 |
| Operating expenses..... ..... ..... | 127,500.00 |
| Yearly profits ..... ..... | $ 45,000.00 |
| Corresponding to a dividend of 32 per cent.[1] | |

The following patents are of smaller importance, but are put in for the sake of completeness.

## SUTHERLAND'S PROCESS.

W. S. Sutherland[2] precipitates metal upon easily fusible forms, to produce surface condensers and steam generators.

## ELMORE'S PROCESS.

F. E. Elmore[3] patented a process for the manufacture of hollow vessels and evaporating pans in which the forms were coated first with a layer of adhering and then with a coating of non-adhering copper. The forms thus treated were then placed upon a horizontal shaft in the bath and connected up as cathodes, using as anodes either copper strips or strips of insoluble material arranged at equal distances from the cathode. The shaft carrying the cathode is rotated and the precipitate is worked by smoothing tools.

[1] The differences in the cost of labor in Europe and in America would modify many of these assumptions.—Translator.

[2] English Patent 8,054, May 22, 1884.

[3] English Patent 10,451, Sept. 3, 1885.

## PROCESS OF DAVIS AND EVANS.

J. W. Davis and J. O. Evans[1] produce hollow metallic ware by using sectional forms upon which the metal is deposited while the electrolyte is circulated in the usual manner.

C. G. Haubold produces perforated hollow metallic cylinders by fastening upon the forms upon which the metal is to be precipitated rods of non-conducting material which on being removed leave a cylinder with corresponding perforations.

## PROCESS OF A. KRUGER.

Miss A. Kruger[2] obtained a patent for the production of flexible objects by the electrolytic precipitation of metal, the several layers of which are separated either partially or totally from each other by intermediate layers so as to be sufficiently flexible in spite of their solidity.

### *Patent Claims.*

1. A process for the production of flexible elastic bodies electrolytically, characterized by producing alternately repeated electrolytic deposits of metal and intermediate layers completely or partially separating the metallic layers from each other.

2. A method of carrying out the process of Claim 1, in which the metallic layers are deposited upon an elastic support in order to produce greater elasticity of the coating.

3. The methods of carrying out the processes of Claims 1 and 2, in which the metallic layers consist of different metals or alloys in any desired order or sequence.

4. A method of carrying out the processes of Claims 1-3, in which the metallic precipitates are smoothed or pressed mechanically.

The process consists practically in the use of various electrolytes and certain changes and sequences for the obtaining of metals and alloys of fixed composition, which later may be caused to unite with each other by heating, and the smoothing of the surface by a suitable smoothing apparatus.

[1] English Patent 8,108, April 20, 1892.

[2] German Patent 95,761, Sept. 20, 1896; English Patent 26,102, Nov. 9, 1897; see also Zeitschrift f. Elektrochemie, 6, 356.

*Examples of the Process.*

As examples are mentioned: In order to produce a body with a screw-like surface a conical hollow spindle of metal is used which is provided with a coating of graphite mixed with spirits of turpentine, which after being completely dried, is smoothed over. By rotating the spindle in an electrolytic bath a thin coating is precipitated, which is smoothed and provided with a separating layer. Then a further metal coating is precipitated in the bath and the manipulation continued in this manner until the desired strength of deposit is reached. In case that a still greater strength of the metal coating is desirable it can be obtained by having direct contact of the separate metallic layers, which is done by drawing well placed lines through the separating layer so that at these points the succeeding metallic deposit comes in contact with the underlying metallic layer, without, however, sensibly affecting the flexibility of the whole.

# XII. MANUFACTURE OF PARABOLIC MIRRORS.

The expensive operations required for the production of exact parabolically curved mirrors has led many investigators to attempt to produce such mirrors electrolytically in a cheaper manner.

## PROCESS OF THE ELMORE GERMAN AND AUSTRO-HUNGARIAN METAL COMPANY, LIMITED, AND P. E. PRESCHLIN.

Amongst the important attempts which have been practically tried we may mention the process of the Elmore German and Austro-Hungarian Metal Company, Limited, and P. E. Preschlin.[1]

*Patent Claims.*

1. An arrangement for the manufacture of saucer-shaped vessels electrolytically characterized by placing the cathode, corresponding to the form of the vessel, upon an inclined axle, in order thereby to place the driving gear and bearings of the axle outside of the bath, while parts of the cathode dip into the bath.

2. In the arrangement of the apparatus described in Claim 1 a smoothing tool pressed by a spring which by means of wheels and levers moves slowly in the plane of the axis of rotation of the cathode in order to act upon all parts of the concave vessel.

## PROCESS OF COWPER-COLES.

Sherard Osborn, Cowper-Coles and the Reflector Syndicate, Limited,[2] have solved the problem of manufacturing perfect mirrors for reflectors in a most characteristic manner

*Patent Claims.*

1. The process for the manufacture of hollow mirrors characterized by covering over a mould with a layer of wax, precipitating upon this layer silver by a chemical process, afterwards pre-

[1] German Patent 71.831, April 6, 1893.

[2] German Patent 89,249, Feb. 26 1896; English Patent 5 600 March 16, 1895.

cipitating upon the silver a layer of palladium galvanically, afterwards also galvanically precipitating a further coating of copper or another suitable metal, while rotating the form, and heating the mirror after removing from the form in order to alloy the palladium with the silver or treating the mirror with a solution of potassium cyanide or the like in order to remove the silver.

2. In the process described in Claim 1, the production of the wax coating by painting with a solution of wax in benzine or any other volatile solvent.

3. In the process of Claim 1, rubbing and polishing the silver coating before the galvanic precipitation of the palladium.

4. In the process of Claim 1, the use of a form consisting of a mixture of sulphur and graphite in which the latter material is somewhat in excess.

*The Forms and Their Manufacture.*

Forms are made out of glass, wax, metal, or any other suitable material which may be provided with a thin coating of silver. It must be noted that the silver coating can be directly precipitated upon the wax; all other kinds of forms must be first coated with a layer of wax before they can be silvered. The wax solution is best as a solution of bees-wax in benzine, because the latter volatilizes very rapidly and leaves the dissolved wax upon the form in an unusually uniform layer. When this coating has become sufficiently solid it is rubbed with a piece of chamois leather until it has a high polished surface. This treatment is quite necessary with glass forms since the small flaws found upon the surface of the same will easily become larger by use, and they cause the formation of still larger unevenness if they are not carefully covered over.

The silver precipitate produced in the chemical way is likewise rubbed and polished with leather, whereby at the same time the silver is loosened from the support. The silvered form is then covered over with palladium in a galvanic bath consisting of

| | |
|---|---|
| Palladium ammonium Chloride ..... | 0.62 per cent. |
| Ammonium chloride ..... | 1.00 " |

The bath is worked at a temperature of 24° C., using graphite plates for anodes. The current density used is 0.027 ampere per

square decimeter, the bath tension corresponding to the feeble concentration of 4 to 5 volts.

The silver bath for coating the wax consists of

| | |
|---|---|
| Silver nitrate | 0.5 per cent. |
| Caustic potash | 0.5 " |
| Glucose | 0.25 " |

The form being thus prepared it is placed in a copper bath containing:

| | |
|---|---|
| Water | 83 parts |
| Copper sulphate | 13 " |
| Sulphuric acid | 3 " |

At starting a high current density is used up to 10 volts tension. The palladium layer is covered over very quickly with copper and then the current density is decreased. During the precipitation of copper the form is continually rotated and the precipitate may be smoothed by smoothing tools while it is forming.

*Loosening of the Precipitate.*

When the copper backing has reached the desired thickness the form with its silver, palladium and copper precipitates is removed from the bath and warmed to between 65° and 95° C., whereupon the layer of wax melts and the form is separated from the precipitate. The precipitate is now further heated in order that the silver may alloy with the palladium, or the silver coating is treated with a solution of potassium cyanide or some other solvent of silver which does not attack the palladium.

In the first case the mirror will have a surface consisting of a palladium-silver alloy which has the advantage that the palladium is not so easily tarnished as the silver while the silver gives to the precipitate a high lustre.

If, on the other hand, the silver is completely dissolved away then a pure palladium surface is left, which likewise shows a high lustre because it was produced upon a polished silver background. Instead of precipitating the palladium upon the silver and copper upon the palladium the copper can be precipitated immediately upon the silver, and the palladium or any other non-tarnishing metal precipitated upon the silver after the removal of the mirror from the form.

If the form is of metal, for instance of iron, with a layer of copper silvered upon its surface, the palladium can at once be precipitated upon its surface without first coating it with silver; the copper can also be precipitated immediately upon the form having a silver coating.

Chromium may serve as a substitute of palladium or silver in the manufacture of spherical mirrors.

The economy of the manufacture of mirrors by the above described process consists principally that the reflectors do not need tedious polishing but at the most need a treatment such as is called in practical galvanoplasty, "Hand coloring." At the same time the mirror surfaces are produced nearer to the mathematically correct shape than by the previously used process. Finally the new mirrors are less sensitive to deformation by uneven heating and are not so easily injured by rough handling.

If desired the reflectors can also be made hollow so that water or any fluid may be run through them to avoid too high heating when in use or the alteration of shape which is caused by heating may be compensated for by unequal thickness of the walls of the reflector.

The forms are made preferably of a mixture of sulphur and graphite, with the latter somewhat in excess, and may be cast in glass moulds.

The palladium or palladium alloy can also be placed upon the mirror in the form of an amalgam, for instance, by a similar process to that used in gilding with mercury.

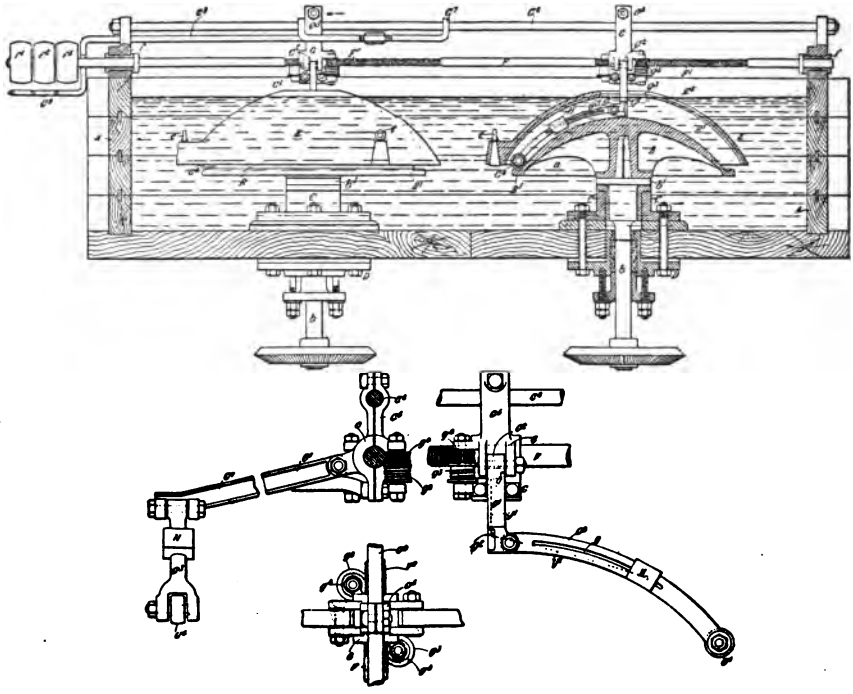
*Apparatus.*

The patent specification describes a series of apparatus particularly for the carrying out of the electrolytic part of the work. Fig. 55 shows a longitudinal section of an electrolytic bath on which the copper background of the mirror is deposited.

Figs. 56-58 show the details of the apparatus.

Inside the box A is the form B serving as cathode and provided with an edge $B^1$ and arranged so as to be removable from but resting upon the square upper end of a vertical shaft *b*, which is rotated by conical wheels beneath through the journal C and the packing box D. The anode E has an arched form corresponding

to the form B and may be hung in the eye *e* in any convenient manner. It is covered inside with a woven cover, for instance of unbleached cotton, in order that any small particles from the anode may not fall upon the form. During the rotation of the form B the roller $G_4$, which is coupled by an arm $G_3$ to an arm $G_1$, produces pressure upon the copper precipitate. This latter lies removable in the yoke G, held there by the eye $G^2$, the end being movable backwards and forwards by the endless screw $F^1$, placed



Figs. 55, 56, 57, 58.

upon an axle F. The axle F is fixed upon the box A by the bearings *f* and carries at one end three disks $f^1$, $f^2$, $f^3$, of which the middle one is loose and driven by one crossed and one straight belt. The belt fork, $G^9$, which governs the position of both belts, is fastened to a bent lever, $G^7$, by means of a rod, $G^8$, and in the same manner as the upward directed arm, $G^5$ moves the nut G upon the rod, $G^6$, which is fastened above the shaft F.

By the arrangement described the direction of rotation of the shaft F is periodically automatically reversed, since the nut G moved in one direction by the screw $F^1$ strikes against the end of the bent lever, $G^7$, with its arm, $G^5$, and moves with it until the belt reversing motion is operated; whereupon the screw moves in the opposite direction until the arm, $G^5$, strikes against the other end of the bent lever and again reverses the belts. The arm, $G^1$, moves with the motion of the nut, G, since it passes into the slit, $E^2$, of the anode E, while the roller, $G^4$, moves up to the apex of the form.

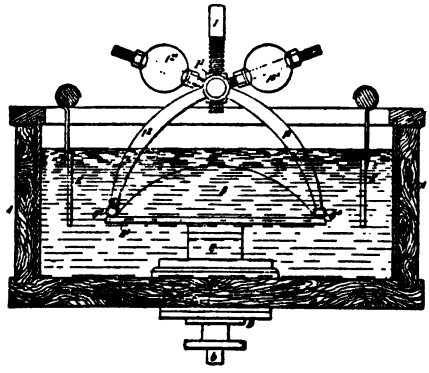


Fig. 59.

In order that the roller, $G^4$, may regulate automatically the pressure which it exerts against the top of the copper precipitate corresponding to the circular part of the mirror upon which it works, the arm, $G^3$, is provided with a weight, H, which is carried in a slit, *g*, and has an automatic motion imparted to it by the arrangement shown in Figs. 56-58. The threaded part, $F^1$, of the shaft F engages the worm wheel, $g^4$, which is keyed to the nut G, and upon whose axle a roller, $g^3$, alternately winds and unwinds a chain or a string, $g^1$, which is carried over an idler, $g^2$, to the rod of the balance weight, H, and thus moves it up and down as the shaft, F, is turned in one or the other direction.

In Fig. 59 there is shown a somewhat different arrangement. The cupola-shaped anode is replaced by two plate-like forms. Two rollers, $G^4$, are placed diametrically opposite each other in the arms $I^2$ and $I^3$ loaded by the weights $I^2x$ and $I^3x$. Both arms

are connected to the nut, $I^1$, which is moved up and down by the vertical spindle, I, whereby the rollers, $G^4$, approach almost to touching each other at the apex and can separate towards the periphery of the form. The nut, $I^1$, is hindered from turning by the rod $I^4$, which may be arranged to be revolvable around the drum, $I^5$, fixed upon the box A, so that the whole arrangement may be swung to one side if the form *b* is to be taken out.

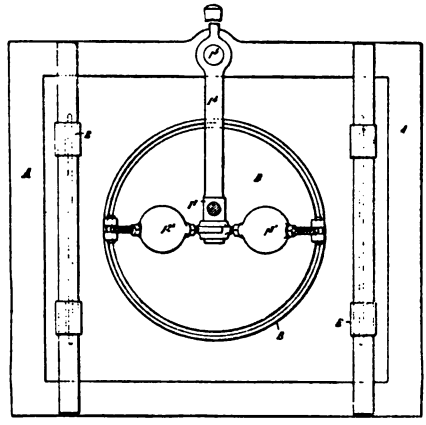


Fig. 60.

Fig. 61 shows another arrangement which can be used in place of that in Fig. 59. The bent arm J is fastened to the side of the containing vessel at $J^1$, its upper end being held by an adjustable brace, $J^2$; its outer form corresponds to that of the mould B. Two

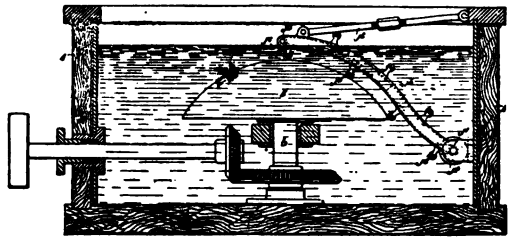


Fig. 61.

chain rollers, $J^3$ and $J^4$, are fastened to the ends of J, one of which is provided with a driving sheave, and carry the chain, $J^5$, upon which are a number of rollers, $J^6$, replacing the pressure roller, $G^4$. The arm J carries a guide for the chain and the pressure

rollers, $J^6$, roll one after the other upon the form B, each describing a path from the periphery to the crown of the mould.

The carriers for the roller axles are so arranged that they can be easily removed if the mould or the completed mirror is to be taken out. The pressure rollers can also be moved by little fingers or eccentrics, especially if the distance between the periphery and crown of the mould is divided between several rollers.

A suitable arrangement is also that of inclining the shaft B, and giving the box an angular cross-section in such manner that one wall is at right angles to the shaft. The shaft B can also be made telescopic and provided with a screw arrangement or the like to allow of the form being lifted out of the box.

The observation of the precipitate is facilitated if the vessel is connected by means of a hose with another vessel so that by the raising or lowering of the latter the solution can be run in or run out of the precipitating box.

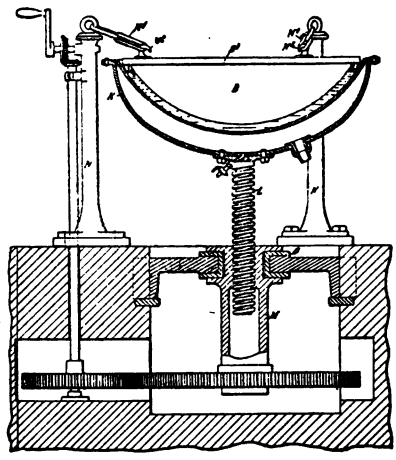


Fig. 62.

Fig. 62 shows an apparatus suitable for the precipitating of a galvanic coating of palladium or chromium upon the form. The pan K is heated with steam and lined with lead or some other metal suitable as an anode and which will hold the palladium solution. It is carried by a spindle L, which since it is prevented from rotating by the steam pipe may be raised or lowered by

means of the nut M turning in the bearing O, so that the form B fastened by means of hooks $N^2$ and the chain $N^1$ to the supports N, can be dipped into the solution by the raising of the pan K or left out of the solution by the lowering of the same. With this arrangement a comparatively small quantity of palladium solution is necessary for constituting the bath.

Instead of the forms as shown in Figs. 55-61 with their bent surfaces arranged on top, these may be inverted and driven by vertical shafts from above. In these cases the round anode and the pressure rollers can be dispensed with and replaced by the pressure of the friction between the surface of the rotating form and the electrolyte.

This process is carried out on a large scale by the "Searchlight Syndicate, Limited,"[1] who manufacture parabolic mirrors and locomotive headlights. Several reflectors are precipitated and taken from one form without the latter needing polishing. The process is not expensive. For instance, the silver deposit does not weigh more than 0.059 milligram per square inch and is 0.0000034 inch thick. The cost of this deposit is not more than 2½ to 4 cents per square inch.

[1] The Electrician, London, (46), 578 to 580.

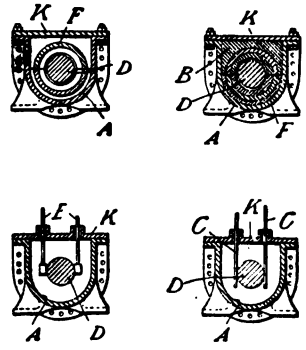
# XIII. MANUFACTURE OF TUBES.

In the processes coming under this heading the most necessary items are suitable arrangements to separate the metal deposited upon suitable mandrils from the same, and to obtain an outer surface smooth and free from excrescences.

Elmore has succeeded in this line quite brilliantly, producing on a larger scale tubes of the most varying diameters and lengths.

For the quick production of tubes of small diameter, J. O. S. Elmore[1] uses the following apparatus suitable for continuous working (Figs. 63-66):

The bath is contained in a trough shaped vessel A, having a *U*-shaped section and divided by partitions into a number of chambers through which the core D passes. In some of these




Figs. 63, 64, 65, 66.

subdivisions the electric current is led to the core by springs C and the precipitate is rubbed by polishing stones B. The anodes are only placed in such compartments which contain neither contact places or smoothing tools, thus avoiding the plating of these parts.

The trough is longer than a single core which latter extends between two rods of non-conducting material such as wood or the like. It is passed through the end of the box by means of stuffing boxes H.

[1] German Patent 95,857, July 2, 1897; English Patent 7,222, April 2. 1896.

The electrolyte flows continuously through the apparatus and the trough is covered with a closely fitting cover R in order that the electrolyte may be conducted through it under pressure. The core is rotated during the action of the process and moves in and out through the chambers.

*Patent Claims.*

1. The apparatus for the manufacture of tubes by electrolytic deposition of metal, characterized by using a box A divided into chambers with a rotating core or mandril D, serving as a cathode

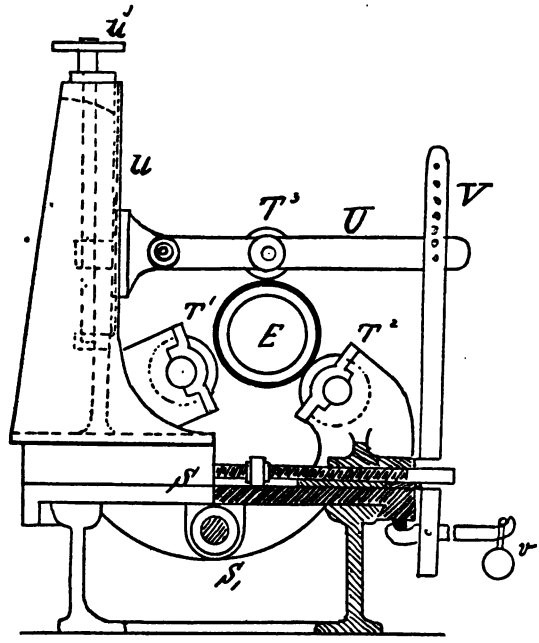



Fig. 67.

and movable backwards and forwards in the direction of its length and provided with contact springs C and smoothing tools *e*, in some of the compartments, and with anodes *f* of the metal to be precipitated surrounding the anode in the alternate compartments, in such manner that the electrical current passes through the contacts C and the anodes, decomposing the electrolyte flowing through the compartment and depositing the metal upon the core.

2. The form of apparatus for carrying out Claim 1, in which a series of vessels A have their cores or mandrils insulated from each other by the insertion of non-conducting pieces, and the anode of each box is in electrical connection with the contact springs bearing upon the mandril of the next following box, thus making it possible to remove from time to time the last mandril, to move up the following mandril into the last box and to place a polished mandril in the first box and so to produce tubes continuously.

*Old Process of 1890.*

The old process[1] for the manufacture of tubes had the following patent claims.

1. The process of producing copper tubes electrolytically consisting in placing the iron mandril first in a copper cyanide bath and coating it with a layer of copper which is afterwards oxidized and subsequently placed in an acid solution of copper sulphate for the purpose of further precipitating and compressing of the copper; using in the latter bath copper plates with granulated cop-

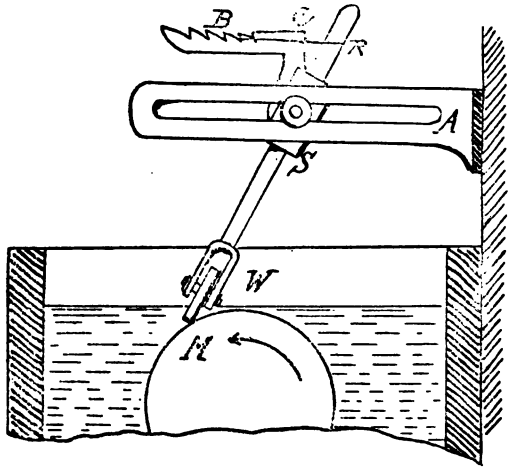



Fig. 68.

per thereupon as anodes, and rotating the mandril serving as cathode, while at the same time the precipitated layer of copper is

[1] German Patent 59,933, Nov. 19, 1890; English Patent 18,896, Nov. 21, 1890; American Patent 464,351; French Patent 209,602,

compressed by an oscillating polishing tool, and finally subjecting the mandril thus coated to the influence of pressure rollers in such manner that the copper coating is stretched in the direction of its circumference, and thus loosened from the mandril.

2. The modification of the process of Claim 1, consisting in afterwards plating a certain thickness of copper, in order to form separated concentric copper tubes one over the other.

3. For the carrying out of the process of Claim 1, the use of two parallel series of electrolytic baths with mandrils therein, the rotation of which is accomplished by means of an intermediate shaft, while the backwards and forwards motion of the polishing tools is produced over all the mandrils simultaneously by means of a reversing pulley and coupling actuated by a finger fastened upon a spindle of the first pair of mandrils.

4. The carrying out of the process described in Claim 1, consisting in the loosening of the copper tubes from the iron mandril by placing the mandrils between concentric rollers and slowly rotating the same while at the same time pressure rollers $T^1$, $T^2$, $T^3$, normal to the tube exert pressure upon the copper tube and are movable in the direction of the length of the tube.

*The Polishing Tools.*

The Elmore process lays particular stress upon the construction of the polishing tools and they patent several different forms. The Elmore German and Austro-Hungarian Metal Company, Limited, makes the smoothing tools in the shape of a wheel rotating upon an axis, which is approximately perpendicular to the rotating mandril. The wheel is moved the length of the mandril backwards and forwards, and at the same time has a rotary motion. As soon as the surface of the precipitated metal becomes uneven the smoothing wheel must have a radius which is smaller than the smallest radius of any of the depressions in the coating. The wheel can then enter into any cavity and work its surface. Fig. 68 shows a section through the bath in which the wheel-formed smoothing tool acts upon the rotating mandril M. A is an arm provided with a screw spindle which moves it backwards and forwards parallel to the axis of the mandril. The smoothing tool is then moved backwards and forwards upon the metallic sur-

face of the deposit. A clamping screw fastens the second arm B to the bracket A by a slot in the latter and the rod R, which is movable by means of the screw S. The rod R is fork-shaped and carries the wheel W, which with one edge runs upon the surface of the mandril. A rubber band C passing around the rod R and into the teeth upon the arm B, serves to press tne wheel W against the circumference of the mandril.

Since the arm B moves back and forth upon the mandril the wheel W passes along the latter and continually forces its edge to the smoothing of new deposits. When one of these edges is dulled the wheel is turned around the axle of the rod R in order to use the other edge. A positive motion can be given to the wheel W by means of a wire or a cord running around a small pulley upon the same axle and so give to the wheel a quicker or slower motion than it would naturally acquire from its contact with the copper tube. The driving wire or cord is stretched the whole length of the bath and is kept tight by a weight so that it continually presses against the small pulley and thus rotates the wheel W.

*Patent Claim.*

An arrangement for the smoothing and compressing of metals, which are being precipitated upon a rotating mandril characterized by using a wheel of agate or a material of approximately equal hardness which is pressed against the mandril with one edge while the latter is rotated and simultaneously moved backwards and forwards along the tube.

An alteration in the manner of smoothing[1] is obtained by giving to the smoothing tools an additional motion lengthwise.

*Patents of Elmore.*

Further improvements in the Elmore process are contained in the following patents:

English Patent, 2,618, February 14, 1889.
German Patent, 65,808, April 12, 1891.
German Patent, 72,195, April 6, 1893.
German Patent, 71,811, April 14, 1893.
German Patent, 77,745, March 4, 1894.

[1] German Patent 67,947, Sept. 29, 1892; English Patent 17,631, Oct. 15, 1891; American Patent 503,076.

*Literature.*

The following articles contain additional information:

El. (1888), **22**, 47.

Lum. el. (1888), **30**, 435; **31**, 280; **32**, 579.

Engineering (1898), No. 1714, William Brown.

El. Rev. (1891), **28**, 449 and 476. Watt.

Engineering (1890), **50**, 21 and 46. A. W. Kennedy.

*Operation.*

In the manufacture of 1,000 kilograms of copper tubes there are used 1,170 kilograms of coal, for a bath tension of 0.5 volts, corresponding to a cost of about $1.75.

At the works of the Elmore Company in Hunsled, near Leeds, there are four dynamos each of 37.5 kilowatts and furnishing 50 volts and 750 amperes.

These works use Chili copper granulated by running into water. The plant contains 60 baths in series each of the dimensions, 3 meters long, 0.8 meter wide and 1 meter deep. The bath tension is 0.9 volt. The precipitate grows slowly so that working night and day a copper tube of 0.3 millimeter thickness requires 6 days for its production. In the works of the German Elmore Company in Sladern, on the Sieg, there are 1,200 HP., of which 550 are used. The dynamos furnish 1,200 amperes at 50 volts. The works can produce 35 tons of tubes weekly. Atmer gives some exact figures of the profits of this process using 94 to 96 per cent. blister copper. The granules are used in a layer 20 centimeters thick upon the anode plate. The tanks are arranged in long double rows in series. Every two rows of tanks possess a common shaft serving for the driving of the mandrils. Between the tanks of each row are cast iron slides lengthwise of the boxes and an automatic mechanism moving in slots in these guides provides the necessary motion for the smoothing tools.

The copper tubes increase in thickness 0.03 of a millimeter between each passage of the agate smoothing tools, thus obviating the precipitation of crystalline copper. The advantage of the smoothing tools is in the fact that using them, current densities up to 1,000 amperes per square meter can be employed. The normal current density on the other hand is scarcely 200 amperes.

The normal length of the tubes is three meters and the process must never be interrupted during the formation of a tube.

The tube being ready the box containing it must be cut out of the circuit, and the solution run into a tank at a lower level in which the anode slime is allowed to settle.

*Loosening of the Tube.*

The loosening of the tubes which are made up to diameters of 1.6 meters is either accomplished in the previously described way or in case copper mandrils are used by substituting for a period of half an hour, for the polishing agate, as long as the precipitate is still quite thin, an agate roller which rolls upon the precipitate with a moderate pressure and thus loosens it from the mandril.

Large copper sheets can be obtained by the Elmore process by cutting a cylinder parallel to the axis of the mandril. The table in the Appendix gives data concerning the weight of tubes thus produced.

## PROCESS OF THE FRENCH COPPER SOCIETY.

The Societe des Cuivres de France[1] produces compact tubes electrolytically.

The smoothing and compressing is attained in this process by using in place of the agate tools of the Elmore process the pressure of two rollers moving upon each other.

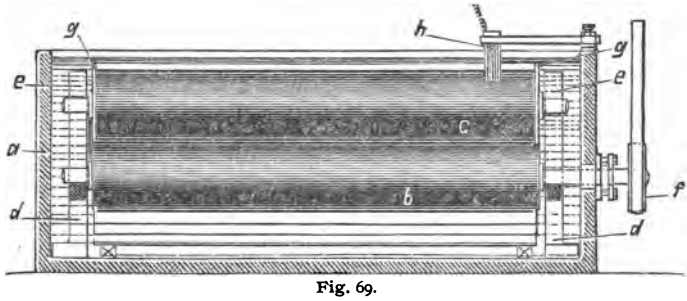



Fig. 69.

*Apparatus.*

The apparatus used for this precipitation is shown in Figs 69-71. The container *a* holds the electrolytic bath and has the roll-formed cathodes *b* and *c* contained in any suitable number in the

[1] German Patent 81,648, April 7, 1894; English Patent 23,680, Dec. 5, 1894; American Patent 538,359, April 30, 1895.

vessel. The lower roller *b* has its axle supported by insulating blocks *d*, which are also provided with guides *e* for the spindle of the upper roll *c*.

The lower roll is driven by a belt pulley *f* and communicates its motion to the upper roll *c* which is held loosely in the bushing in order that it can change its position according to the increase of the thickness of the precipitate. The rolls are kept together either by their own weight or by springs. At the beginning, however, the rolls should not touch because such would injure the graphite coating upon them. In order, therefore, to provide contact between the rolls from the start they are provided with copper disks at their ends having a slightly larger diameter than the rolls so that these come in contact with each other and leave the rolls thus uninjured.

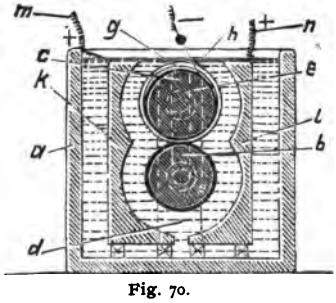



Fig. 70.

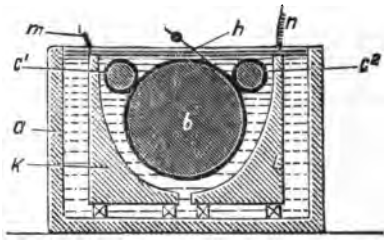



Fig. 71.

When a precipitate of a certain thickness has formed the copper rings alluded to are taken off and the rolls allowed to come in contact with each other. The current is carried to the rolls by brushes *h* touching the roll *c*. The rolls, instead of being arranged as in Fig. 69, can be arranged in any desired number, as in Fig. 71.

The sectional shape of the anodes *k l*, as well as their material, is determined by the shape of the cathodes and by the material to be deposited.

The current entering at *m* and *n* precipitates the copper uniformly upon the rolls *b* and *c*, and is cut off as soon as the desired thickness of deposit has been obtained.

*Large Tubes.*

In precipitating larger tubes according to this process, two or more smaller rolls can be used in order to avoid too large dimensions of the tanks and these rolls are arranged as shown in Fig. 71. The current is carried into one of the rolls *b* by a brush *h*, and passes to the rolls $c^1$ and $c^2$. Thus tubes of large or small diameter may be produced simultaneously in the one vessel.

As in the Elmore process the tubes can be either used as such or by slitting and straightening as copper sheets.

*Patent Claims.*

1. The process for the electrolytic deposition and simultaneous compressing of copper and other metals characterized by the use of two or more rotating rollers as cathodes in such manner that they exert pressure upon each other in order to compress the metal precipitating upon them.

2. The apparatus for carrying out the process of Claim 1, consisting of a vessel *a*, in which adjacent or superposed rolls, *c*, or *b*, $c^1$, $c^2$, always in light contact with each other, are arranged as rotating cathodes, their distances from each other being automatically regulated according to the thickness of the metal deposit, and the anodes have any suitable form.

## PROCESS OF DUMOULIN.

The Dumoulin process[1] was discovered in 1895, in an attempt to find a suitable method of avoiding the excrescences upon an electrolytic deposit. Dumoulin observed, as many others have likewise, that the deposition of metal occurred principally on the projecting parts of the cathode and that these excrescences were the principal reason that ordinary cathode copper cannot be rolled. If the projecting excrescences are, however, insulated until the surrounding part has reached the same thickness, or if a diaphragm is interposed between the excrescences and the solution, then the precipitation will finally arrive at a point where again the smooth surface begins to be deposited upon.

Dumoulin obtains this hindering of precipitation upon the excrescences by bringing the cathode cylinder into contact with an

[1] German Patent 84,834, April 9, 1895; English Patent 16,360, Aug. 31, 1895; Zeitschr. f. Elektrochemie, **2**, 509.

insulating or adhesive material placed upon a porous body. The coating of the body with insulating material occurs only upon the projecting parts, thereby hindering further deposition upon them. Fatty substances are the most suitable as coating material or such bodies which naturally contain fatty substances or with which such can be mixed. Amongst these may be mentioned, animal membranes and extracts from them (albumen, fibrin, etc.), skins, muscles, entrails, and the like. In general, any sort of material may be used which is saturated with a fatty or oily insulating body. The principal requirement is always that the body is pliable and does not fall to pieces in the machine.

In the special treatment proposed by Dumoulin, the following points play an important part:

1. The contact surfaces of the cathode and the rubber holding

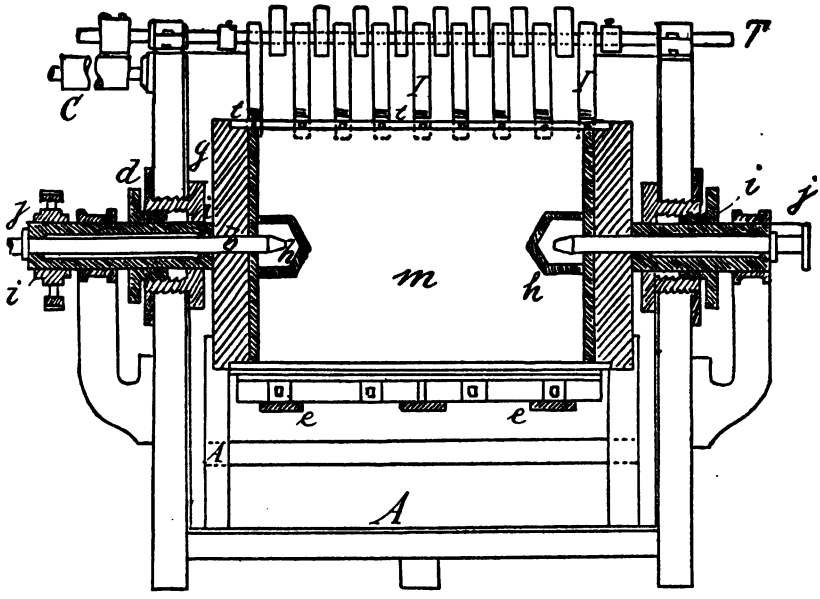



Fig. 72.

the insulating material.

2. The pressure of the rubber.
3. The velocity of motion of the cathode or of the rubber.
4. The current density.

The rubber is given a slight longitudinal motion in order that all parts of the cathode can be equally treated; the movement of the rubber is independent of the cathode cylinder.

*The Apparatus.*

Fig. 72 shows in section the principle of the apparatus; it shows more particularly a longitudinal section of the apparatus for the manufacture of large tubes and sheets. The core *m*, upon which the cathode is placed, is in this case made short. At the ends it has a pulley *g* of insulatating material, and in the recesses of the mandril, there are rectangular bearing pieces *h*, which are connected with the spindle *b*. The latter passes through hollow bearings *i*, which are fastened by stuffing boxes to the vessel A. The electric current is led in by contact brushes *j*.

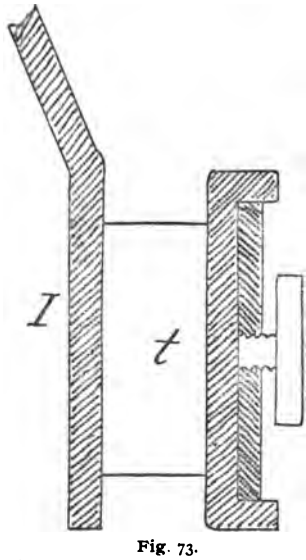



Fig. 73.

For larger tubes the mandril is of brass or bronze, for small tubes of steel. The mandrils are polished or greased before they are put into the baths. In order that all points on the surface may be equally coated with the fatty material the rubber is moved parallel to the length of the cathode cylinder by means of a screw. This motion must be adjusted to the velocity of rotation of the cylinder and be uniform.

### *The Rubber.*

Fig. 73 shows the rubbing apparatus for applying the fatty material. The latter is placed in it and pushed against the cathode. The rubbing surfaces are arranged along side of each other upon a shaft T, (Fig. 72), upon which they are moved by a worm gear C. They are movable upon the shaft T, but not longitudinally.

Dumoulin has the opinion that the insulating material can also be put directly in the bath; in this case the rubbers would have the function only of passing over the cylinder and rubbing the insulating material upon the projections of the cathode. In such cases brushes of silk or the like would suffice.

### *Loosening of the Tubes.*

The loosening of the tubes is attained by slowly warming them, whereby the mandrils separate from the precipitate; if this is insufficient, hydraulic pressure is used.

It is of importance for the process that the temperature does not exceed 16° C., in order to insure the permanence of the animal membranes used. The temperature can be kept down by the blowing in of air and circulation of the electrolyte, at the same time iron and organic compounds would be thereby oxidized.

### *Patent Claim.*

The process for the manufacture of uniform electrolytic metallic deposits characterized by placing upon the cathode during the precipitation insulating materials in such manner that only the projecting parts of the precipitate receive a coating of the insulating material, the process being in this respect similar to the inking of type by ink during printing, by which treatment and in which process also the insulating material is oxidized in the bath and can be removed by a rubbing arrangement used for applying the insulating material as soon as the projecting parts have disappeared and become uniform with the whole surface of the cathode and for that reason do not need longer the application of the insulating material for the retardation of the deposition upon them.

*Operation.*

The Dumoulin process is carried on at the Brunoy Works, near Paris, and at Widnes, England, by the Electrical Copper Company, which has a capital of $2,500,000.[1]

In the latter works there are 5 dynamos furnishing a total current of 1,300 amperes at 75 volts. The electrolyte used is a solution containing 40 per cent. of copper sulphate with 7 per cent. of sulphuric acid. The tanks are wooden vessels with lead linings and the electrolyte circulates through thirty in series. The mandrils are copper cylinders 3.6 meters long and 40 centimeters in diameter, which dip half way into the electrolyte. The anodes are of cast blister copper in the shape of a U. The current density is 3.5 to 4 amperes per square decimeter and the bath tension 1.6 volts.

[1] Wm. Brown, El. Rev. (1898), **43**, 561, 663. Engineer, Oct. 21, 1898.

# XIV. ELECTROLYTIC ETCHING.

Practical electrochemistry has not only utilized the cathodic reactions of electrolysis, but also anodic reactions in order to produce useful articles of the most different kinds. The process of dissolving metals at the anode which is partially protected or covered with a design, has been known for a long time, and somewhat recently the process of Joseph Rieders of electrolytically etching dies deserves to be mentioned more at length. This process is called by the inventor electro-engraving, and is described in full in the next chapter.

Concerning the ordinary etching processes, such solutions are used as electrolytes which contain free anions, such as are able when discharged against the metal of the anode to form an easily soluble salt therewith, but which do not show a particular tendency to attack the anode when current is not passing. The choice of the electrolyte should not be difficult to the chemist or electrochemist. For copper or its alloys dilute sulphuric acid or alkaline salts, such as potassium sulphate or potassium nitrate; for iron and zinc, sodium sulphate or ammonium chloride, for silver potassium cyanide in solution, etc.

The procedure in electrolytic etching consists in coating the object to be etched with lacquer, melted stearine or some other insulating material, laying bare the parts of the metal to be engraved or etched, cleaning the latter with alcohol, benzine, lime, or any suitable cleaning material, but in such a manner that the insulating coating is not injured. The article thus prepared is used as an anode in the etching bath. For cathode a metallic or carbon plate is used. On closing the circuit the metal is dissolved at the exposed places, while the covered places remain unattacked. By regulating the current it is possible to etch more or less deeply or to accelerate the process.

This method has many applications; so there can be imagined an imitation of deep engraving processes carried out by printing a sample upon the metallic surface with a grease color, in which

case the fat in the color serves as a coating. The design which is to be engraved remains uncovered. The printed surface is then covered with powdered asphalt or some sort of a resin, some of which sticks to the greasy places while it can be blown away from the unprinted places. The object being then warmed to the melting point of the resin or asphalt, the latter melts, and after cooling serves as a protective coating, while the uncovered metallic surfaces are being etched, so that in this way a deeply cut design is obtained. It is possible, further, to deposit in the depressions so etched a precipitate of a metal of different color from the ground mass, and upon polishing the whole plate to have a beautiful piece of inlaid work.

In this manner, also, may be produced, without difficulty, plates and rolls for calico printing and embossing of paper, cloth, leather, etc., which have been formerly made at great expense by engraving.

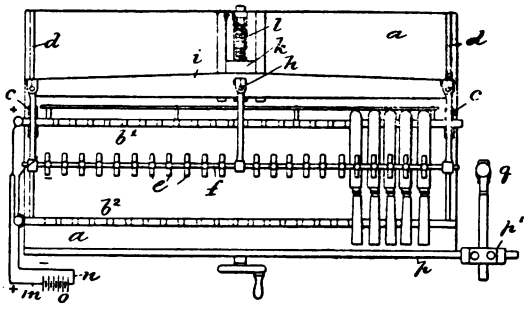


Fig. 74.

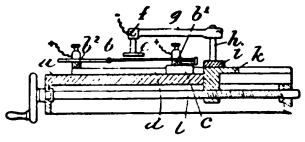


Fig. 75.

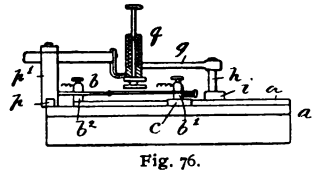


Fig. 76.

## BURDETTE'S PROCESS.

Burdette[1] patented a process for the galvanic etching, suitable for producing figures, monograms, numbers, and other designs upon cutlery, tableware, etc. Figs. 74-76 show his apparatus.

[1] German Patent 83,615, Feb. 26, 1895; Zeitschr. f. Elektrochemie 2, 359.

The working table *a*, usually of wood, has a holder *b* for receiving the articles to be etched. The holder consists in this case of rods $b^1$ $b^2$, with shallow depressions in their surfaces for receiving and holding the pieces. Since the process is particularly intended for the etching of cutlery, although it is applicable for the etching of all other kinds of metallic objects, its application to table knives is taken as an illustration.

The rods $b^1$ $b^2$ are of metal and insulated, and lie upon strips with the insulating material fastened to the conductors *d*. The detachable metallic conductor is arranged at some distance above the point where the drawing or the like is to be etched. In the apparatus shown in Fig. 74 these conductors are of small copper strips carried by a rod *f*. The rod *f* is fixed to the arm *g*, which projects from the stand *h*, fastened to the slide *i*. The slide is fastened to the conductor *k*, which is movable in relation to the row of knives by means of a screw spindle *l*. This form of apparatus is suitable for the treating of a number of pieces, such as knives, to produce the same mark or design upon all. For other pieces any suitable form of slide can be used. It is necessary that the conductor remains a certain time immediately above the surface of the piece, being treated in order to etch in the mark by the action of the electric current.

The conducting wire *m* goes from the positive pole *o* of the source of electricity through the rods $b^1$ $b^2$, upon which the articles to be etched are laid, while the conducting wire *n* from the negative pole is connected with the rod *f* carrying the conductor *e*. In a suitable place, for instance, along the front edge of the table, there is a guide *p*, upon which is fasteened a movable sliding block $p^1$, which carries an adjustable arm with the stamp *q*. This stamp when pressed down upon the surface of the knife-blades prints upon them the design to be etched, the blades having been previously coated with a special material: the surface of the stamp is cleaned with a solution which will be described. After the articles have been stamped one after the other, the stamp is moved sideways, the slide forwards, and the conductors arranged directly above the imprint of the stamp upon the blades.

The etching is completed by using a current which acts upon the imprinted design, but leaves untouched the background.

The material for the protecting coating consists of

| | |
|---|---|
| Naphtha | 1 liter |
| Carbon bisulphide | 125 grams. |
| Pulverized resin | 2000 grams. |
| Cupric chloride | 1500 grams. |

A thin layer of this coating is placed upon the surface, the stamp washed off with a weak solution of caustic potash, and then pressed upon the coated surface. The articles are then washed with water and the imprint of the stamp with a weak solution of ammonium chloride. The articles are then at once subjected to the electrolytic etching. The imprint of the stamp is etched upon the metal because the place stamped is in conducting connection with the current used. The ammonium chloride used in this process can be replaced by common salt.

*Applications.*

The process, as described, takes only a short time. When the etching is completed the knives are taken out, dipped into a solution of caustic potash or soda in order to dissolve off the coating. The knives are then ready for further treatment.

The process described allows of etching to a sufficient depth to show quite clearly the design of the stamp.

## HALL AND THORNTON'S PROCESS.

Hall and Thornton[1] have invented another method of applying anodic action in order to produce points upon metallic rods.

Many metals are injured by the cutting, turning, hammering or rolling which they must undergo in order to put them into the desired shape.

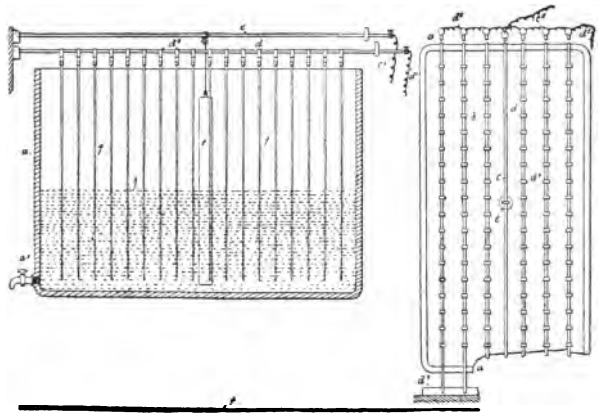
Unavoidable heating of surfaces which are being worked can easily draw the temper of steel pieces. To avoid this some factories have replaced grinding by an electrolytic bath in which the articles to be worked are used as anodes in order to be thus reduced to the desired thickness. In the process being described articles of uniform or non-uniform dimensions may be treated and the desired removal of material is controlled by raising or lowering the level of the electrolyte or by the corresponding sinking or raising of the articles. The articles treated are awls, need-

[1] German Patent 87,845, Aug. 30, 1895; see also Zeitschrift f Elektrochemie 3, 13

les, surgical instruments, fish hooks, umbrella ribs, rapiers, swords, spokes for bicycles, forks, etc. The patent describes the following apparatus for the carrying out of this process.

*Apparatus.*

Fig. 77 shows the apparatus for the treatment of a series of wire rods, which are to be given a tapered form by being gradually lifted out of the solution. Fig. 78 is a plan of the arrangement of Fig. 77. Fig. 79 shows a tapered metallic rod produced



Figs. 77, 78, 79.

by this process. Fig 80, the same before being treated. Fig. 81 is a cross-section on a large scale of the connections for one of the ends of the rod.

Fig. 80.

Fig. 81.

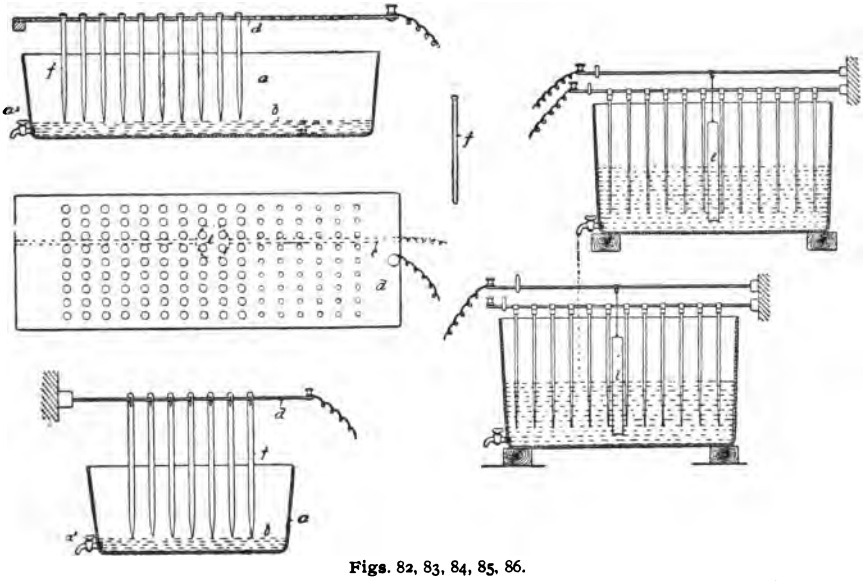
The holder $a$ contains the electrolyte or the dissolving fluid $b$, and metallic zinc is added to the same, if necessary; $a_1$ is a stopcock for running off the solution. $c$ and $d$ are conductors of the current. The conducting pieces, $c_1$ $d_1$, carry the current from the negative or the positive pole of the electric generator to $c$ and $d$, while the contacts $d_2$ are connected to the rods $d$, their ends lying upon insulating pieces, $d_3$. Upon the rods $d$ are yokes $d_4$ to which are fastened the upper ends of the hanging rods $f$, which form

the anodes, while the negative rod *c*, which is likewise insulated at one end is in connection with a block of carbon *e*, which forms the electrode. The electric current enters the solution at the anode rod *e* and leaves the solution at the carbon cathode.

When rods or wires of iron are to be used the solution becomes saturated with that metal which either deposits as slime or is deposited upon the cathode. Instead of using only one carbon block as cathode a series of such blocks may be used connected with the negative conductor of the system.

Fig. 82 shows the invention applied to the pointing of metallic pins, needles, or the like. Fig. 83 is a plan of Fig. 82. Fig. 84 shows a needle before being pointed. Fig. 85 shows how needles, having eyes, can be hung in order to be pointed by the process.

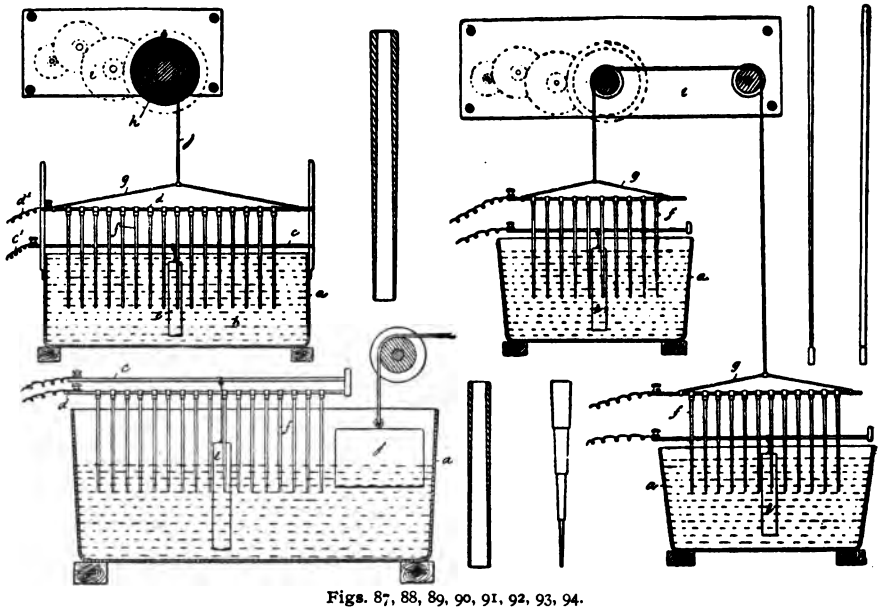
*a* is the containing vessel, $a_1$ the run off cock, and *f* the articles to be pointed by being gradually drawn out of the solution *b*. *d* is a positive conductor and holder or the pieces, while *e* is the cathode which is hung to the other conductor *c*.



Figs. 82, 83, 84, 85, 86.

Fig. 86 shows a sectional diagram of the apparatus applied to simultaneously carrying out the process in two vessels in one of which the fluid rises, while in the other it sinks.

Fig. 87 shows an apparatus in which the articles to be pointed are gradually lifted out of the solution, the level of the fluid being kept constant.



Figs. 87, 88, 89, 90, 91, 92, 93, 94.

*a* is the containing vessel in which the carbon block *e* is hung, forming the cathode and connected with the negative conductor *c*, *f* are the articles to be treated connected to the positive rod *d* of the frame *g*. The rising and sinking of the frame is done by the spring *j*, or a similar contrivance fastened to the pulley and whose motion can be regulated by a clockwork or other mechanism *i*.

Fig. 88 shows a process intended for the simultaneous use of two vessels and in which the objects are alternately dipped into one vessel and raised out of the other.

*a* are the holders, *g* the frames, and *i* the regulating arrangement, *f* the objects to be treated fastened to the frames. As one frame is raised out of the liquid the other one sinks into the liquid.

Fig. 89 shows a further form of the apparatus in which the change of level of the liquid is attained by the rising and lowering

of a displacement block *j*. The movement of this block is either regulated by clockwork or by other means and produces a corresponding rise and fall of the liquid so that the objects dip more or less into the solution.

Fig. 90 shows a tapered umbrella rib or bicycle spoke with an enlargement allowed to remain at the end for the forming of a head or other purpose.

Fig. 91 shows the original form of this rib or spoke with a nick at the point where the tapered end and the head come together.

Fig. 92 shows a tube, the inner and outer surfaces of which are tapered by this process.

Fig. 93 shows a tube which is tapered only on the inside.

Fig. 94 finally shows a rod tapered in sections obtained by allowing the fluid to remain stationary at the level where the offsets are to be made, or by correspondingly arresting the motion of the solution at these points.

# XV. ELECTROLYTIC ENGRAVING.

## INTRODUCTION.

We have already said that this process is one in which the work of the engraver is replaced by the use of the electric current. It has been principally developed by Joseph Rieders[1]. So far, it has principally been applied to engraving on metals, and of these principally on iron and steel.

We will go somewhat into the subject of metal-engraving in order that the information to be given may be better understood.

There are to be distinguished three kinds of metallic engraving. The oldest application of this work was concerned with ornamenting useful objects in order to increase their commercial value. This original creative application of the engraving art was characteristic of the early times. The second division of the engravers work was concerned with the finishing of the reliefs which had been made by casting; we call this work chasing and the artist a chaser or engraver. The third group finally is concerned with the manufacture of plates for printing which we call copper or steel engravings. While it would not appear that the electrolytic engraving could revolutionize the field of engraving, as above described, yet it may become a valuable aid in that part of the engraving which is concerned with printing, at least by the use of which objects may be made or embellished by the use of pressure. Electrolytic engraving is for this reason of importance for this part of the engraving because it replaces expensive hand labor by which dies and moulds must be worked from the crude piece of steel.

For a long time the engraving art has hoped to find in electrolytic engraving a rational means of replacing the artistic work of the engraver by that of the ordinary workman. The work of Jacobi in the field of copper galvanoplastics raised the general

[1]Electrochemische Zeitschrift. 1, 1900; Dr. G. Langbein, Zeitschr. f. Elektrochemie, 4, 139; 6, 328; German Patent 124,529, Feb. 20, 1900; Supplementary to German Patent 95,081, Feb. 7, 1897.

hope that the further pursuit of this line would lead to favorable developments for the engraver. But up to the present it has not become practicable to produce electrolytically deposits of steel of such physical qualities as ordinary steel; quite aside from the fact that the production of heavy iron precipitates, such as are required in coinage dies takes an enormous length of time. But if galvanoplastics is to find use in the coinage industry it can only be in the form of steel galvanoplastics. But the galvanic steel precipitate lacks toughness in spite of the fact that its hardness is nearly equal to that of steel; this is partly due to the absence of carbon in the iron precipitated, which is the characteristic ingredient of steel.

## ENGRAVING WITH PARTIAL COVERING.

If there is no possibility that electrolytic precipitation can come to the aid of the coming art, yet in electrolytic engraving there is a possibility of producing stamping dies electrolytically. The above described etching methods were only in a few rare cases

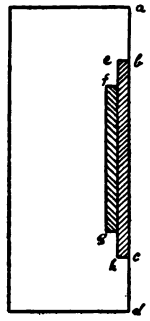



Fig. 95.

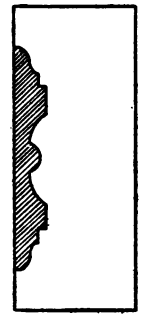


Fig. 96.

applicable to the coining industry. If for instance, Fig. 95 represents a section of an iron plate with the surfaces *ab* and *cd* covered, then the surface *bc* can be etched. If we afterwards cover the surface *bef* and *chg* we can obtain a second etching within the limits *fg;* or altogether we obtain the form *befghc.* This process is for example practically used in the manufacture of etched cliches. In Fig. 96 if it is desired to etch out the form as figured it would be necessary to coat over very restricted areas in order to obtain approximately the shape desired. The rounded parts

in particular could not be thus etched out and would have to be engraved by hand; the workman on which must actually be an artist in order to finish the design.

## ELECTRO-ENGRAVING PROCESSES.

We will now pass to the electro-engraving processes themselves of such nature that the use of coverings are completely dispensed with. The process is based upon the fundamental principle that for the attainment of the end sought it is completely immaterial whether the places not to be etched are covered over or whether the places to be etched only come in contact with the etching bath. The inventor allows the insulation to be done by a layer of air and attains this end by producing, by means of a porous material, a fluid surface which by successive forward movements will come more and more into contact with the metal until a reversed relief is entirely in contact with the metal surface. This will be clear from an inspection of Fig. 97. The vessel is filled with am-

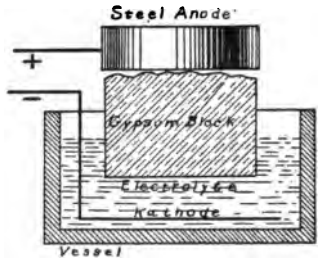



Fig. 97.

monium chloride solution which may be regarded as the electrolyte. The plaster block is intended to take the engraving to the steel anode above. The cathode described by the inventor as a wire spiral is placed underneath the gypsum block. As soon as the plaster block is saturated with the electrolyte its upper surface becomes in reality the upper surface of the electrolyte in relief, acting as the attacking agent against the steel anode; the surface of the plaster being solid prevents the pressure of the steel block from altering the surface of the electrolyte so that the steel comes only in contact with the electrolyte at the high places of the plaster relief. The current being then turned on, the chlorine liber-

ated at the anode dissolves iron which diffuses as ferric chloride, $FeCl_3$, into the pores of the plaster. The weight of the steel anode presses down on the points in relief upon the plaster block as soon as any appreciable thickness of the steel is dissolved and the continuance of this pressure brings the anode and plaster block into better and better contact until the whole of the plaster block is in contact with the steel anode.

## RIEDER'S FIRST INVESTIGATIONS.

In his first attempts with this process Rieder used a steel plate 3 mm. thick and his electrolyte a 10 per cent. solution of ammonium chloride. The battery had a tension of 2 volts. The weak point of this arrangement was that the operation of the etching process could not be followed, since by taking up and again replacing the steel block points of contact were changed.

After this the course of the process was guessed at. After about one hour's electrolysis it was found that a black mud appeared at the steel anode, after the removal of which the details of the relief were to be recognized. It was, therefore, necessary to devise an arrangement which would allow the mould and the steel anode to be separated during the process in order to be able to clean the anode. A quite simple model apparatus was devised by which much better results were obtained, from which Rieder adduced the following fundamental laws of procedure:

### *Fundamental Laws.*

1. The carbon contained in the steel and possibly also other admixtures insoluble in the electrolyte, must be mechanically removed from the anode plate from time to time since they lie as a powder between the plate and the model making exact work impossible. The intervals at which this must be done is primarily dependent on the amount of carbon in the steel to be etched.

2. The ammonium chloride at the surface of the plaster block is quickly used up, and since the diffusion through the pores of the plaster is much slower than in a free fluid the amount of ammonium chloride available at the surface is far below that required by the process. This condition requires the occasional removal of the steel block at intervals dependent upon the relative size of the etching surface and the current strength used. The

current density in order to work as fast as possible is used as high as conditions will permit and taking this into consideration it was found that 20 seconds is the maximum interval of working which must not be exceeded.

*Behavior of the Steel Anodes.*

The black mass mentioned above which lies between the steel plate and the plaster block is not only carbon but largely ferrous oxide. It seems that as soon as the chlorine at the surface of the plaster model is used up there is no longer electrolysis of ammonium chloride, but decomposition of water takes place. The oxygen thus liberated at the anode forms with the iron an insoluble ferrous oxide which deposits upon the anode and stops the etching. The evolution of gases at the anode also expels electrolyte from the etching surface and produces irregularities in the etching.

*The Plaster Used.*

Rieder met many difficulties in finding the most suitable composition for the plaster blocks. At first he used alabaster plaster, which, however, had the great inconvenience that as soon as it was saturated with electrolyte it became extremely easily injured as soon as the anode was let down upon it. It was hardly possible to find a substitute for plaster since the other self-hardening materials do not have the porosity which makes gypsum so suitable for this process. Rieder made investigations, by altering the relative weights of water and plaster used to find such a composition which would be durable and yet porous. Another device appeared to be that of making several similar models which could replace each other as soon as one was injured; but this met with the difficulty of placing the models always in exactly the same position. He afterwards succeeded by using a special method of casting the plaster, which in combination with satisfactory tests upon mixtures used gave quite good results.

*Mechanical Devices.*

Fig. 98 shows some of the mechanical apparatus of the process, *g* is a glass vessel with the lid *d* having an offset on which is placed the plaster model *E* surrounded by a rubber mantel *C*. It

may be interesting to remark here the manner in which it is possible to replace the plaster blocks in the later machines. Several rubber mantels *c* are made in which the similar models are cast so that they are fastened in the cover in exactly the same posi-

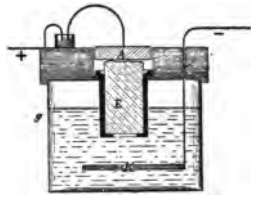



Fig. 98.

tion, to which end a mark is made upon the cover.

The anode to be etched is at *A*. This was an exactly cylindrically turned steel plate prevented from turning sideways by a pointer not shown in the figure. The anode fits exactly into the opening of the cover *d*.

The apparatus had to be converted into an automatically working machine, which was done by the firm of Dr. G. Langbein & Company, of Leipsic, as shown in Fig. 99. The description is briefly as follows: The plaster mould is fastened by two conical wedges into the cast iron frame upon a vertically moving table, the latter worked by an eccentric. Above this table is the clamping plate to hold the steel anode to be etched. The clamping plate is likewise adjustable and can be fastened exactly parallel to the mould by a suitable adjustment. A carriage having a rotating brush and movable by an eccentric cleans off the steel plate, the brushes being washed off by water, while, besides a sponge roller is carried over the mould for the purpose of wetting it with electrolyte.

### *Action of the Machine.*

The mould upon the movable table is applied to the plate to be etched without shock and as elastically as possible; after being in contact 15 seconds and during which electrolysis takes place the mould is lowered from contact with the anode and the cleaning processes by the brushing and sponging rollers take place. As soon as the cleaning appliances have been withdrawn the mould is again brought against the steel plate and the operation repeated.

For each machine there is a mould casting arrangement, in which the frames of the machine are cast into place.

*The Dynamo.*

The dynamo used gives a tension of 12 volts to 15 volts and the current used for a plate 200 x 300 mm. is about 50 amperes, if

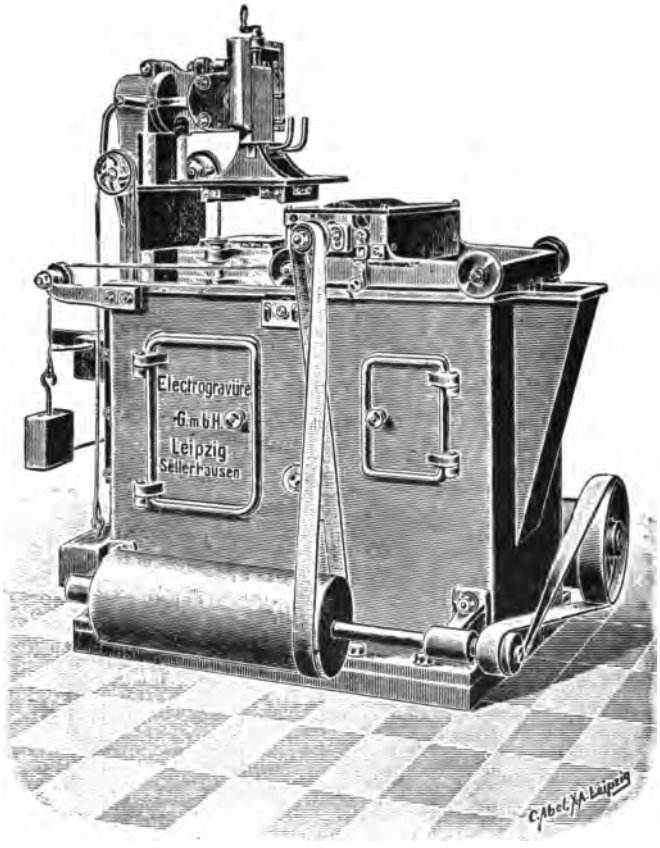



Fig. 99.

the whole surface of the plaster model comes into contact with the steel plate. An electrolytic engraving plant of this kind was exhibited at the Paris Exposition in 1900.

*Duration of the Etching.*

According to the depth of the etching the operation may take

more or less time, about 4 or 5 hours being required for a depth of 1 mm., varying somewhat with the fineness of the model. The cleaning of the same can, if desired, be accomplished with the assistance of compressed air. If the duration of etching is 12 seconds, some 600 to 800 etching periods must be used in order to etch to the depth of 1 mm.

*Patent Claims.*

German Patent, 95,081, February 7, 1897.

1. The process of forming reliefs and other shapes electrolytically by using a negative in the shape of a porous mass, such as plaster, clay, or the like, cast or cut, using the article to be formed as anode pressing lightly upon the forming side of the porous block saturated with a suitable electrolyte, and a cathode immersed in the electrolyte.

2. The apparatus for the carrying out of the process of Claim 1, consisting of a porous block upon which is a negative of the design to be produced and whose forming surface rests with a light pressure against the anode to be formed, and which is saturated with electrolyte; the block being further encased in an encasing mantel and the position of the anode being assured by guides.

German Patent, 124,529, February 20, 1900; an addition to the previous patent.

1. A device for the carrying out of the process of forming reliefs and other designs electrolytically according to patent 95,081, consisting in placing the negative upon a vertically moving table above which is the anode so that when the table is lowered in the manner provided, a slide carrying a cleaning brush for the anode can pass between the negative and the anode, while a moistening roller supplies the porous block with fresh electrolyte in order to counteract the alkalinity of the electrolyte upon the surface of the negative.

2. An apparatus for the carrying out of the purposes of Claim 1, characterized by means for automatically raising the negative by means of a lever as the etching proceeds.

*Manufacture of the Machines.*

The manufacture of electro-engraving machines is in the hands

of the Elektrogravure G. m. b. H., in Leipsic, and we take from the catalogue of this firm the following data concerning the machines, their listing and price:

| Machine. No. | Engraving of Surface m.m. | Necessary for Etching. Volts. | Amperes. | Total Power used: H. P. | Price of the complete installation. |
|---|---|---|---|---|---|
| $E_0$ | 50 × 50 | 15 | 2 — 3 | 0.40 | $ 625.00 |
| $E_1$ | 120 × 150 | 15 | 15 | 1.00 | 1125.00 |
| $E_2$ | 200 × 300 | 15 | 30 | 1.35 | 1725.00 |
| $E_3$ | 350 × 450 | 15 | 60 | 2.50 | ——— |

The air compressor is only used when engravings deeper than 3 mm. are to be made. When engraving not so deep the cleaning by means of the brush and sponge roller suffices. The price given above includes the air compressor and the power data includes its power consumption. If the air compressor is not used the price of the machine and its power requirement is as follows:

| For machines. | $E_1$. | $E_2$. | $E_3$. |
|---|---|---|---|
| Deduct from price .... | $100.00 | $125.00 | $150.00 |
| Deduct from power .... | 0.5 | 0.75 | 1.0 H. P. |

In the price for these plants the cost of the dynamo is not included, but the license for using the German Patent goes with the machine, good for the use of the machine during the life of the patent.

*Auxiliary Apparatus.*

The necessary conditions for the carrying out of electro-engraving is the possession of an original model of wax, plaster, wood, etc., from which the necessary plaster moulds needed for the electro-engraving can be reproduced in numerous duplicates. For these purposes a complete plant must contain the following auxiliary apparatus.

Two casting apparatus for 20 frames; one drying oven for drying the plaster moulds rapidly, arranged for burning spirits, petroleum, or gas.

*Plant for Electro-Engravure.*

Fig. 100 shows the ground plan for the erection of an electro-engraving plant of a capacity indicated in the table by the figure $E_2$. Such a plant has been erected in Moscow by the Faberge Silverware House.

*Cost of Making Dies.*

The cost of making finished electro-engraved dies depends upon the depth of etching and the dimensions of the mould. It also depends on whether the engraving is to be afterwards engraved or

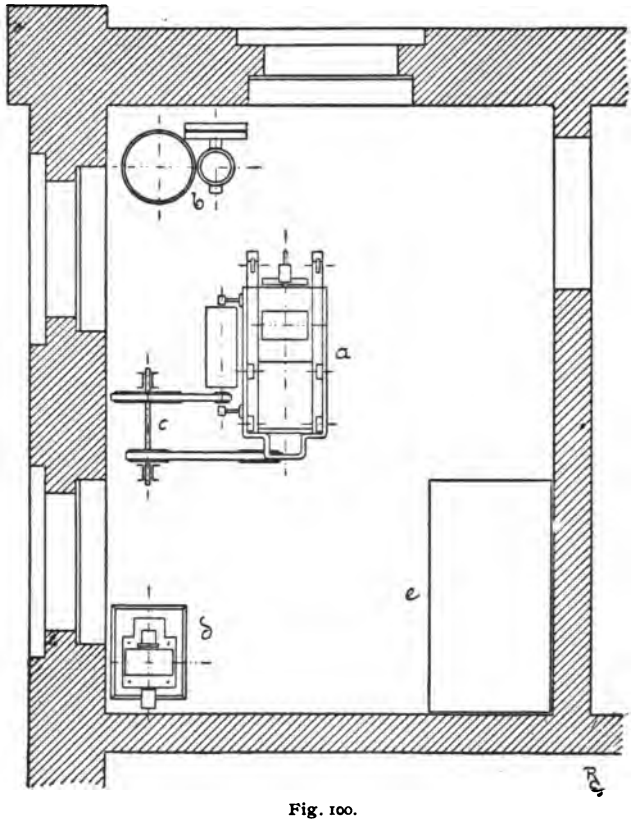



Fig. 100.

chased, or whether it is to be ready for use when it comes from the machine.

*Profits.*

The approximate estimate of the profits of an electro-engraving plant have been made as follows by the author:

The machine of the size, $E_2$, will produce about 10 dies at once having a maximum etched depth of 2 millimeters. These dies

are quite fine work, which, if made by hand, would be worth $37.50 apiece.

FIXED PLANT.

| | |
|---|---|
| 1 Electro-engraving machine, $E_2$, having a maximum engraving surface of 200 × 300 mm., including air compressor | $ 1750.00 |
| 1 dynamo machine, 30 amperes, at 15 volts, including shunt regulator, ammeter, voltmeter, and switch | 125.00 |
| Shafting, pulleys and small appliances | 125.00 |
| Total investment in plant | $ 2000.00 |

COST OF PRODUCING TEN DIES.

| | |
|---|---|
| Power, 10 days of 10 hours each; equals 150 H. P. hours at 1½c. per H. P.-hour | $ 2.25 |
| 1 engraver for touching up the dies at $1.50 per day | 15.00 |
| 1 moulder and 1 engineer for 10 days | 21.25 |
| 150 kilos of steel at $20 per 100 kilos | 30.00 |
| 10% sinking fund on the capital invested for 10 days | 6.67 |
| 5% interest on capital for 10 days | 3.33 |
| Government tax 50% on the wages | 13.13 |
| Cost of producing 10 stamps | $ 94.12 |

PROFITS.

| | |
|---|---|
| Value of produce (one die per day 200 × 300 mm.) per year of 300 working days | $ 11250.00 |
| Cost of 300 dies according to the above assumption | 2823.65 |
| Leaving as yearly profit | $ 8426.35 |

Corresponding to a dividend of 420 per cent.

It may be said that these figures make no claim to be true since very much depends on the cost of labor for running the machine. The profits must be smaller when work is produced which must compete with cheap hand labor. With increasing fineness of the work, however, the cost of manufacturing them by hand increases rapidly and the profits of the electro-engraving process will increase when producing such fine work.

# APPENDIX.

## TABLE I.

### STRENGTH TESTS OF GALVANOPLASTICALLY FORMED COPPER PRINTING PLATES.

| Number of test. | Composition of the bath. $CuSo_4$ | $H_2SO_4$ | % | Current density in amp. per sq. diam. | Direction in which test strip was taken. | Dimensions of the strip before testing. Width. | Thickness. | Length of the test piece. | Absolute strength. I. Elastic Limit. | II. | Elongation to the I. Elastic Limit. | II. | After breaking. Permanent Elongation. | Contracted area. Original area = 1. | Hardness, determined by length of groove made by a falling Weight of 0.612 kg. Dropping. 50 mm. | 100 mm. | Remarks. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Kg. per sp. centi.[1] | | | | % | | | | |
| 1 | | | | 0.61 | | | 0.71 | | 2838 | 739.5 | 950.5 | 0.062 | 0.082 | 27.0[5] | 0.607 | 6.6 | 7.9 |
| 2 | | | | 1.00 | | | 0.74 | | 3270 | 845 | 1080.5 | 0.070 | 0.090[5] | 22.5[5] | 0 677 | 6.2 | 7.5 |
| 3 | 20 | 4 | | 1.25 | | | 0.74 | | 3378 | 776.5 | 1047 | 0.067 | 0.093 | 17.6 | 0.643 | 6 | 7.2 |
| 4 | | | | 1.67 | | | 0.80 | | 3605.5 | 625.5 | 938.5 | 0.051 | 0.080 | 16.6 | 0.619 | 6.2 | 7.5 |
| 5 | | | | 2.22 | | | 0.73 | | 3724.5 | 754 | 925 | 0.056 | 0.073 | 16 | 0.643 | 5.7 | 6.9 |
| 6 | | | | 0.85 | | | 0 79[5] | | 2855 | 692.5 | 880.5 | 0.030 | 0.070 | 30.9 | 0.596 | 6 4 | 7.9 |
| 7 | 17 | 7 | | 1.50 | | | 0.75 | | 3619.5 | 566.5 | 733 | 0.041 | 0.055[5] | 27.5[5] | 0 622 | 6.6 | 7.9 |
| 8 | | | | 0.85 | | | 0.84 | | 2517 | 714 | 833 | 0 056 | 0.064 | 14 9[6] | 0.836 | 6.7 | 8.2 |
| 9 | 14 | | | 1.50 | | | 0.86 | | 3238 | 552 | 843 | 0.042[5] | 0.072[5] | 20.2 | 0 533[5] | 5.9 | 7.3 |
| 10 | | | | 0.85 | | | 0.84 | | 2500 | 714 | 952 | 0.053 | 0.073[5] | 6.1 | 0.889 | 6.7 | 8 |
| 11 | 10 | 7 | | 1.50 | | | 0.84[5] | | 3532 | 710 | 975 | 0.058 | 0.085[5] | 10.3 | 0.752 | 5.9 | 7 |
| 12 | | | | 1.00 | | | 0.86[5] | | 2715 | 520 | 866.5 | 0.043 | 0.076 | 26.4 | 0.642[5] | 7 | 8.1 |
| 12 | | | | 1.00 | | | 0.801 | | 2440.5 | 482 | 748.5 | 0 044 | 0.054 | 5.7 | 0.807[6] | 6.8 | 8.1 |
| 13 | 20 | 4 | | 1.50 | | | 1.227 | | 2941 | 509 | 855.5 | 0.046 | 0.080 | 26.4 | 0 541[5] | 6.8 | 8.1 |
| 14 | | | | 2.50 | | | 0.847[5] | | 2949.5 | 472 | 678.5 | 0.036[5] | 0.059 | 25.1 | 0.667[5] | 7.1 | 8.4 |
| 15 | | | | 4.00 | | | 1.64 | | 2404.5 | 489 | 716.5 | 0.044 | 0.068 | 19.4[5] | 0.663[5] | 6.7 | 7.9 |
| 16 | | | | 1.00 | | | 1.12[6] | | 2738 | 444 | 664.5 | 0 037 | 0.058[5] | 33.0[5] | 0.520[5] | 7.1 | 8.4 |
| 17 | 15 | 3 | | 1.50 | | | 1 012 | | 2795.5 | 517.5 | 727.5 | 0.043[5] | 0.074[5] | 28.5[5] | 0.560[5] | 6.9 | 8 |
| 18 | | | | 3.23 | | | 0 42 | | 3013 | 513 | 820 | 0 035 | 0.063 | 19.4 | 0.685 | 6.1 | 7.9 |
| 19 | 10 | 2 | | 1.00 | | | 0.69 | | 2674 | 464 | 753 | 0.036[5] | 0.062[5] | 31.5 | 0.486[5] | 6.6 | 7.7 |
| 20 | | | | 1.50 | | | 0.598 | | 2803.5 | 401.5 | 772 | 0.027[5] | 0.061[5] | 17.2[5] | 0.762[5] | 6.6 | 7.8 |
| 21 | 5 | 1 | | 1.30 | | 50 | 0.60[5] | 150 | 2760.5 | 364 | 596 | 0.023 | 0.041[5] | 19.7[5] | 0.720[5] | 7 | 8.2 |
| 22 | 20 | 4 | | 1.00 | | | 1.93 | | 2802.5 | 583 | 849.5 | 0.052 | 0.077 | 12.5 | 0.827 | 7 | 8.1 |
| 23 | | | | | | | | | | | | | | | | | |
| 23 | | | 0 | 0.25 | | | 0.805 | | 2540 | 571.5 | 961.5 | 0.042 | 0.084[5] | 1.8 | 0.971[5] | 6.5 | 7.8 |
| | | | | | | | 0.79[5] | | 2534 | 503 | 981 | 0.041 | 0.085 | 1 | 0.987 | 6.6 | 7.8 |
| 24 | | | | | | | 1.55 | | 4230 | 733 | 921 | 0.049 | 0.054 | 1.5 | 0 442 | 6.7 | 7 |

Cold saturated.

Fresh, clear bath.

Old bath used a long time.

Maximum current strength with a 5 per cent. bath.

Addition of 6 per cent. zinc sulphate.

Plates made in a Daniell cell apparatus.

Rolled and cold-hammered commercial copper engraving plates

[1] 1,000 Kg per square centimeter = 14,300 pounds per square inch.

## TABLE II.

### CONDUCTIVITY OF ELECTROLYTES WHICH ARE USED IN THE MANUFACTURE OF METALLIC OBJECTS.[1]

The table refers to temperature of solutions of 18° C.

$P$ = percentage by weight of anhydrous salt in the solution.

$\eta$ = number of gram-equivalents of salt in a cubic centimeter of solution.

$S$ = specific gravity of the solution at 18° C., or at 15° C., compared with water at 4° C.

$\varkappa_{18}$ = conductivity of the solution in reciprocal ohms per cubic centimeter $\left(\frac{1}{\Omega}\right)$ at 18° C.

The temperature coefficient gives in fractional parts of $\varkappa_{18}$ the alteration of $\varkappa$ for one degree, for which is taken the mean alteration between 18° and 26°.

Interpolated values are in parenthesis.

| Elektrolyt | $P$ % | $1000\,\eta$ $(m:1/v)$ | $S$ $t/_4$ | $10_4\varkappa_{18}$ | $\frac{1}{\varkappa_{18}}\left(\frac{d\varkappa}{dt}\right)_{22}$ |
|---|---|---|---|---|---|
| $CuSo_4$ | 2.5 | 0.321 | 1.0246 | 109 | 0.0213 |
| | 5. | 0.658 | 1.0531 | 189 | 0.0216 |
| | 10. | 1.387 | 1.1073 | 320 | 0.0218 |
| | 15. | 2.194 | 1.1575 | 421 | 0.0231 |
| | 17.5 | 2.631 | 1.2003 | 458 | 0.0236 |
| $ZnSO_4$ | 5 | 0.651 | 1.0509 | 191 | 0.0225 |
| | 10 | 1.371 | 1.1069 | 321 | 0.0223 |
| | 15 | 2.169 | 1.1675 | 415 | 0.0228 |
| | (20) | 3.053 | 1.2323 | 468 | 0.0241 |
| | 25 | 4.040 | 1.3045 | 480 | 0.0258 |
| | (30) | 5.124 | 1.3788 | 444 | 0.0273 |
| $FeSO_4$ | — | 0.5 | 1.0344 | 154 | 0.0218 |
| | — | 1 | 1.0692 | 258 | 0.0218 |
| | — | 2 | 1.1375 | 390 | 0.0223 |
| | — | 3 | 1.2018 | 461 | 0.0231 |
| | — | 3.56 | 1.2359 | 470 | 0.0243 |
| $NiSO_4$ | — | 0.5 | 1.0379 | 153 | 0.0231 |
| | — | 1 | 1.0759 | 254 | 0.0227 |
| | — | 2 | 1.1503 | 385 | 0.0241 |
| | — | 3 | 1.2219 | 452 | 0.0250 |
| $AgNO_3$ | 5 | 0.307 | 1.0422 | 256 | 0.0218 |
| | 10 | 0.641 | 1.0893 | 476 | 0.0217 |
| | (15) | 1.006 | 1.1404 | 683 | 0.0215 |
| | 20 | 1.407 | 1.1958 | 872 | 0.0212 |
| | (25) | 1.847 | 1.2555 | 1058 | 0.0210 |
| | (30) | 2.332 | 1.3213 | 1239 | 0.0209 |
| | (35) | 2.872 | 1.3945 | 1406 | 0.0207 |
| | 40 | 3.477 | 1.4773 | 1565 | 0.0205 |
| | (45) | 4.158 | 1.5705 | 1716 | 0.0204 |
| | (50) | 4.926 | 1.6745 | 1856 | 0.0205 |
| | (55) | 5.791 | 1.7895 | 1984 | 0.0206 |
| | 60 | 6.764 | 1.9158 | 2101 | 0.0209 |

[1] The figures are mostly taken from the work of Kohlrausch and Holborn, "Das Ceitvermögen der Elektrolyte," 1898.

| Elektrolyt | $P$ % | 1000 $\eta$ ($m$:1/$v$) | $S\,l/_4$ | $10^4 x_{18}^{\circ}$ | $\frac{1}{x_{18}}\left(\frac{dr}{dl}\right)_{18}$ |
|---|---|---|---|---|---|
| $Na_2SO_4$ (Kohlrausch 8, 1879) | 5 | 0.735 | 1.0450 | 409 | 0.0236 |
| | 10 | 1.536 | 1.0915 | 687 | 0.0249 |
| | 15 | 2.411 | 1.1426 | 886 | 0.0256 |
| (Klein 1886) | | 0.5 | 1.0302 | 298 | 0.0241 |
| | | 1. | 1.0602 | 508 | 0.0242 |
| | | 2. | 1.1179 | 800 | 0.0250 |
| $MgSO_4$ | 5 | 0.873 | 1.0510 | 263 | 0.0226 |
| | 10 | 1.836 | 1.1052 | 414 | 0.0241 |
| | 15 | 2.891 | 1.1602 | 480 | 0.0252 |
| | (20) | 4.054 | 1.2200 | 476 | 0.0269 |
| | 25 | 5.342 | 1.2861 | 415 | 0.0288 |
| $(NH_4)_2SO_4$ Kohlrausch 8, 1879) | 5 | 0.778 | 1.0292 | 552 | 0.0215 |
| | 10 | 1.601 | 1.0581 | 1010 | 0.0203 |
| | 20 | 3.337 | 1.1160 | 1779 | 0.0193 |
| | 30 | 5.322 | 1.1730 | 2292 | 0.0191 |
| | 31 | 5.528 | 1.1787 | 2321 | 0.0191 |
| $NH_4Cl$ | 5 | 0.948 | 1.0142 | 918 | 0.0198 |
| | 10 | 1.923 | 1.0289 | 1776 | 0.0186 |
| | 15 | 2.924 | 1.0430 | 2596 | 0.0171 |
| | 20 | 3.952 | 1.0571 | 3365 | 0.0161 |
| | 25 | 5.003 | 1.0710 | 4025 | 0.0154 |
| | | | $t = 15$ | | |
| $KCN$ | 3.25 | 0.506 | 1.0154 | 527 | 0.0207 |
| | 6.5 | 1.029 | 1.0316 | 1026 | 0.0193 |
| $H_2SO_4$ (Kohlrausch 3, 1896) Äquiv. $= \frac{H_2SO_4}{2}$ | 5 | 1.053 | 1.0331 | 2085 | 0.0121 |
| | 10 | 2.176 | 1.0673 | 3915 | 0.0128 |
| | 15 | 3.376 | 1.1036 | 5432 | 0.0136 |
| | 20 | 4.655 | 1.1414 | 6527 | 0.0145 |
| | 25 | 6.019 | 1.1807 | 7171 | 0.0154 |
| | 30 | 7.468 | 1.2207 | 7388 | 0.0162 |
| | 35 | 9.011 | 1.2625 | 7243 | 0.0170 |
| | 40 | 10.649 | 1.3056 | 6800 | 0.0178 |
| | (45) | 12.396 | 1.3508 | 6146 | 0.0186 |
| | 50 | 14.258 | 1.3984 | 5405 | 0.0193 |
| | (55) | 16.248 | 1.4487 | 4576 | 0.0201 |
| | 60 | 18.375 | 1.5019 | 3726 | 0.0213 |
| | 65 | 20.177 | 1.5577 | 2905 | 0.0230 |
| | 70 | 23.047 | 1.6146 | 2157 | 0.0256 |
| | 75 | 25.592 | 1.6734 | 1522 | 0.0291 |
| | 80 | 28.25 | 1.7320 | 1105 | 0.0349 |
| | 85 | 30.90 | 1.7827 | 980 | 0.0365 |
| | 90 | 33.34 | 1.8167 | 1075 | 0.0320 |
| | 95 | 35.58 | 1.8368 | 1025 | 0.0279 |
| | | | $t = 18$ | | |
| $H_3BO_3$ (Bock 1887) Äquiv. $= \frac{H_3BO_3}{3}$ | 0.776 | 0.377 | 1.0029 | 0.022 | 0.0231 } for 18° |
| | 1.92 | 0.936 | 1.0073 | 0.11 | 0.0143 } for 18° |
| | 2.88 | 1.409 | 1.0109 | 0.21 | 0.0111 } for 18° |
| | 3.612 | 1.771 | 1.0131 | 0.31 | 0.0075 } for 18° |

## TABLE III.

SPECIFIC RESISTANCE OF A CUBE OF ELECTROLYTE ONE DECIMETER ON A SIDE. (OHMS).

| 1000 $\eta$ (m). | $H_2SO_4$. | $CuSO_4$. | 1000 $\eta$ (m). | $H_2SO_4$. | $CuSO_4$. |
|---|---|---|---|---|---|
| 0.001 | 277.0 | 1000.0 | 0.1 | 4.444 | 22.2 |
| 0.002 | 143.0 | 527.0 | 0.2 | 2.337 | 12.8 |
| 0.005 | 58.8 | 244.0 | 0.3 | 1.587 | 9.35 |
| | | | 0.5 | 0.976 | 6.49 |
| 0.01 | 32.2 | 139.0 | 1.0 | 0.504 | 3.875 |
| 0.02 | 17.5 | 76.9 | 2 0 | 0.273 | 2.497 |
| 0 03 | 12.2 | 58.8 | 3.0 | 0.199 | 2 083 |
| 0.05 | 7.87 | 38.5 | 5.0 | 0.148 | .... |
| | | | 10.0 | 0.143 | .... |

## TABLE IV.

WEIGHTS OF COPPER PRECIPITATES OBTAINED FROM ACID SOLUTIONS.

| Current density used. | Weight of a square decimeter of the precipitate in grams after | | | |
|---|---|---|---|---|
| Amp. per sq. dm. | 1 hour. | 2 hours. | 5 hours. | 10 hours. |
| 0.5 | 0.59 | 1.18 | 2.96 | 5.92 |
| 0.75 | 0.89 | 1.78 | 4.44 | 8.87 |
| 1.00 | 1.18 | 2.36 | 5.92 | 11.84 |
| 1.25 | 1.48 | 2.96 | 7.40 | 14.80 |
| 1.50 | 1.78 | 3.56 | 8.88 | 17.76 |
| 1.75 | 2.07 | 4.14 | 10.37 | 20.74 |
| 2.00 | 2.37 | 4.74 | 11.85 | 23.70 |
| 2.25 | 2.67 | 5.34 | 13.33 | 26.65 |
| 2.50 | 2.96 | 5.92 | 14.80 | 29.60 |
| 2.75 | 3.26 | 6.52 | 16.28 | 32.55 |
| 3.00 | 3.55 | 7.10 | 17.75 | 35.50 |
| 3.5 | 4.15 | 8.30 | 20.75 | 41.50 |
| 4.0 | 4.74 | 9.48 | 23.70 | 47.40 |
| 4.5 | 5 32 | 10.64 | 26.60 | 53.20 |
| 5.0 | 5.90 | 11.80 | 29.50 | 59.00 |
| 5.5 | 6.50 | 13.00 | 32.50 | 65.00 |
| 6.0 | 7.10 | 14.20 | 35.50 | 71.00 |
| 6.5 | 7.70 | 15.40 | 38.50 | 77.00 |
| 7.0 | 8.30 | 16.60 | 41.50 | 83.00 |
| 7.5 | 8.90 | 17.80 | 44.50 | 89.00 |
| 8.0 | 9.45 | 18.90 | 47.25 | 94.50 |
| 8.5 | 10.05 | 20.10 | 50.25 | 100.50 |
| 9.0 | 10.70 | 21.40 | 53.50 | 107.00 |
| 9.5 | 11.25 | 22.50 | 56.25 | 112.50 |
| 10.0 | 11.80 | 23.60 | 58.00 | 118.00 |

## TABLE V.

### THICKNESS OF COPPER PRECIPITATES.

| Current density used. | Number of hours required for a thickness of | | | | | | | | | | Thickness of the copper precipitate in 10 hours in millimeters. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0.1 mm | 0.2 mm | 0.3 mm | 0.4 mm | 0.5 mm | 0.6 mm | 0.7 mm | 0.8 mm | 0.9 mm | 1.0 mm | |
| 0.5 | 15.1 | 30.2 | 45.3 | 60.4 | 75.5 | 90.6 | 105.7 | 120.8 | 135.9 | 151.0 | 0.0664 |
| 0.75 | 10.1 | 20.2 | 30.6 | 40.4 | 50.5 | 61.2 | 71.0 | 80.8 | 90.9 | 101.0 | 0.0995 |
| 1.00 | 7.5 | 15.0 | 22.5 | 30.0 | 37.5 | 45.0 | 52.0 | 60.0 | 67.5 | 75.0 | 0.133 |
| 1.25 | 6.0 | 12.0 | 18.0 | 24.0 | 30.0 | 36.0 | 42.0 | 48.0 | 54.0 | 60.0 | 0.166 |
| 1.50 | 5.0 | 10.0 | 15.0 | 20.0 | 25.0 | 30.0 | 35.0 | 40.0 | 45.0 | 50.0 | 0.199 |
| 1.75 | 4.3 | 8.6 | 12.9 | 17.2 | 21.5 | 25.8 | 30.1 | 34.4 | 38.7 | 43.0 | 0.233 |
| 2.00 | 3.75 | 7.5 | 11.25 | 15.0 | 18.75 | 22.5 | 26.25 | 30.0 | 33.75 | 37.5 | 0.267 |
| 2.25 | 3.35 | 6.7 | 10.05 | 13.4 | 16.75 | 20.1 | 23.45 | 26.8 | 30.15 | 33.5 | 0.299 |
| 2.50 | 3.00 | 6.0 | 9.00 | 12.0 | 15.00 | 18.0 | 21.00 | 24.0 | 27.00 | 30.0 | 0.332 |
| 2.75 | 2.75 | 5.5 | 8 25 | 11.0 | 13.75 | 16.5 | 19.25 | 22.0 | 24.75 | 27.5 | 0.366 |
| 3.00 | 2.5 | 5.0 | 7.5 | 10.0 | 12.5 | 15.0 | 17.5 | 20.0 | 22.5 | 25.0 | 0.399 |
| 3.5 | 2.15 | 4.3 | 6.45 | 8.6 | 10.75 | 12.9 | 15.5 | 17.2 | 19.35 | 21.5 | 0.466 |
| 4.0 | 1.88 | 3.76 | 5.64 | 7.52 | 9.4 | 11.28 | 13.16 | 15.04 | 16.92 | 18.75 | 0.534 |
| 4.5 | 1.65 | 3.3 | 4.95 | 6.6 | 8.25 | 9.9 | 11.55 | 13.2 | 14.85 | 16.5 | 0.598 |
| 5.0 | 1.5 | 3.0 | 4.5 | 6.0 | 7.5 | 9.6 | 10.5 | 12.0 | 13.5 | 15.0 | 0.664 |
| 5.5 | 1.35 | 2.7 | 4.05 | 5.4 | 6.75 | 8.1 | 9.45 | 10.8 | 12.15 | 13.5 | 0.732 |
| 6.0 | 1.25 | 2.5 | 3.75 | 5.0 | 6.25 | 7.5 | 8.75 | 10.0 | 11.25 | 12.5 | 0.798 |
| 6.5 | 1.15 | 2.3 | 3.45 | 4.6 | 5.75 | 6.9 | 8.05 | 9.2 | 10.35 | 11.5 | 0.864 |
| 7.0 | 1.08 | 2.16 | 3.24 | 4.32 | 5.4 | 6.48 | 7.56 | 8.62 | 9.72 | 10.75 | 0.930 |
| 7.5 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 | 8.0 | 9.0 | 10.0 | 1.000 |
| 8.0 | 0.93 | 1.86 | 2.79 | 3.72 | 4.6 | 5.58 | 6.51 | 7.44 | 8.32 | 9.33 | 1.065 |
| 8.5 | 0.88 | 1.76 | 2.64 | 3.52 | 4.4 | 5.28 | 6.16 | 7.04 | 7.92 | 8.83 | 1.126 |
| 9.0 | 0.83 | 1.66 | 2.49 | 3.32 | 4.15 | 4.98 | 5.81 | 6.64 | 7.72 | 8.33 | 1.200 |
| 9.5 | 0.79 | 1.58 | 2.37 | 3.16 | 3.9 | 4.74 | 5.53 | 6.32 | 7.06 | 7.9 | 1.260 |
| 10.0 | 0.75 | 1.50 | 2.25 | 3.0 | 3.75 | 4.50 | 5.25 | 6.0 | 6.75 | 7.5 | 1.330 |

The numbers in the above table are only true for homogeneous current distribution and do not apply to edges or like cases where the current distribution may have various values.

## TABLE VI.

### AUXILIARY TABLE FOR USE IN THE MANUFACTURE OF COPPER WIRE.

| For wires of a diameter in millimeters of | Surface of one meter length in square decimeters. | Current required for one meter length at a current density in amperes per square decimeter of | | | |
|---|---|---|---|---|---|
| | | 0.5 | 1.0 | 1.5 | 2.0 |
| 1 | 0.31 | 0.15 | 0.30 | 0.45 | 0.60 |
| 2 | 0.62 | 0.30 | 0.60 | 0.90 | 1.20 |
| 3 | 0.93 | 0.45 | 0.90 | 1.35 | 1.80 |
| 4 | 1.24 | 0.60 | 1.20 | 1.80 | 2.40 |
| 5 | 1.55 | 0.75 | 1.50 | 2.25 | 3.00 |
| 6 | 1.86 | 0.90 | 1.80 | 2.70 | 3.60 |
| 7 | 2.17 | 1.05 | 2.10 | 3.15 | 4.20 |

## TABLE VII (a).

WEIGHT OF SEAMLESS COPPER TUBES PER RUNNING METER IN KILOGRAMS. (MADE BY THE ELMORE PROCESS).

| Inside diameter in mm | Thickness of wall in millimeters. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 mm | 1¼ mm | 1½ mm | 1¾ mm | 2 mm | 2½ mm | 3 mm | 3½ mm | 4 mm | 5 mm |
| 3 | **0.11** | **0.15** | **0.19** | **0.23** | **0.28** | **0.39** | **0.51** | **0.64** | — | — |
| 4 | .14 | .18 | .23 | .28 | .34 | .46 | .59 | .74 | — | — |
| 5 | .17 | .22 | .28 | .33 | .40 | .53 | .68 | .84 | **1.02** | — |
| 6 | .20 | .26 | .32 | .38 | .45 | .60 | .76 | .94 | .13 | **1.55** |
| 7 | .23 | .29 | .36 | .43 | .51 | .67 | .85 | **1.04** | .24 | .70 |
| 8 | .25 | .33 | .40 | .48 | .56 | .74 | .93 | .14 | .36 | .84 |
| 9 | .28 | .36 | .44 | .53 | .62 | .81 | **1.02** | .24 | .47 | .98 |
| 10 | .31 | .40 | .49 | .58 | .68 | .88 | .10 | .34 | .58 | **2.12** |
| 11 | .34 | .43 | .53 | .63 | .73 | .95 | .19 | .43 | .70 | .26 |
| 12 | .37 | .47 | .57 | .68 | .79 | **1.02** | .27 | .53 | .81 | .40 |
| 13 | .50 | .30 | .61 | .73 | .85 | .07 | .36 | .63 | .92 | .54 |
| 14 | .42 | .54 | .66 | .78 | .90 | .17 | .44 | .73 | **2.04** | .69 |
| 15 | .45 | .57 | .70 | .83 | .96 | .24 | .53 | .83 | .15 | .83 |
| 16 | .48 | .61 | .74 | .89 | **1.02** | .31 | .61 | .93 | .26 | .97 |
| 17 | .51 | .64 | .78 | .93 | .07 | .38 | .70 | **2.03** | .37 | **3.11** |
| 18 | .54 | .68 | .83 | .98 | .13 | .45 | .78 | .13 | .49 | .25 |
| 19 | .57 | .72 | .87 | **1.03** | .19 | .52 | .87 | .23 | .60 | .39 |
| 20 | .59 | .75 | .91 | .08 | .24 | .59 | .95 | .33 | .71 | .53 |
| 21 | .62 | .79 | .95 | .13 | .30 | .66 | **2.04** | .42 | .83 | .68 |
| 22 | .65 | .82 | **1.00** | .17 | .36 | .73 | .12 | .52 | .94 | .82 |
| 23 | .68 | .86 | .04 | .22 | .41 | .80 | .20 | .62 | **3.05** | .96 |
| 24 | .71 | .89 | .08 | .27 | .47 | .87 | .29 | .72 | .17 | **4.10** |
| 25 | .73 | .93 | .12 | .32 | .53 | .94 | .37 | .82 | .28 | .24 |
| 26 | .76 | .96 | .17 | .37 | .58 | **2.01** | .46 | .92 | .36 | .38 |
| 27 | .79 | **1.00** | .21 | .42 | .64 | .08 | .54 | **3.02** | .50 | .52 |
| 28 | .82 | .03 | .25 | .47 | .70 | .16 | .63 | .12 | .62 | .66 |
| 29 | .85 | .07 | .29 | .52 | .75 | .23 | .71 | .22 | .73 | .81 |
| 30 | .88 | .10 | .34 | .57 | .81 | .30 | .80 | .31 | .84 | .95 |
| 31 | .90 | .14 | .38 | .62 | .87 | .37 | .88 | .41 | .96 | **5.09** |
| 32 | .93 | .17 | .42 | .67 | .93 | .44 | .97 | .51 | **4.07** | .23 |
| 33 | .96 | .21 | .46 | .72 | .98 | .51 | **3.05** | .61 | .18 | .37 |
| 34 | .99 | .25 | 51 | .77 | **2.04** | .58 | .14 | .71 | .30 | .51 |
| 35 | **1.02** | .28 | .55 | .82 | .09 | .65 | .22 | .81 | .41 | .66 |
| 36 | .05 | .32 | .59 | .87 | .15 | .72 | .31 | .91 | .52 | .80 |
| 37 | .07 | .35 | .63 | .92 | .20 | .79 | .39 | **4.01** | .64 | .94 |
| 38 | .10 | .39 | .67 | .97 | .26 | .86 | .48 | .11 | .75 | **6.08** |
| 39 | .13 | .42 | .72 | **2.02** | .32 | .93 | .56 | .21 | .86 | .22 |
| 40 | .16 | .46 | .76 | .07 | .37 | **3.00** | .65 | .30 | .98 | .36 |
| 41 | .19 | .49 | .80 | .11 | .43 | .07 | .73 | .40 | **5.09** | .50 |
| 42 | .22 | .53 | .84 | .16 | .49 | .14 | .82 | .50 | .20 | .64 |
| 43 | .24 | .56 | .89 | .21 | .54 | .22 | .90 | .60 | .32 | .79 |
| 44 | .27 | .60 | .93 | .26 | .60 | .29 | .99 | .70 | .43 | .93 |
| 45 | .30 | .63 | .97 | .31 | .66 | .36 | **4.07** | .80 | .54 | **7.07** |
| 46 | .33 | .67 | **2.01** | .36 | .71 | .43 | .16 | .90 | .65 | .21 |
| 47 | .36 | .70 | .06 | .41 | .77 | .50 | .24 | **5.00** | .77 | .35 |
| 48 | .38 | .74 | .10 | .46 | .83 | .56 | .33 | .10 | .88 | .49 |

| Inside diameter in mm | Thickness of wall in millimeters. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 mm | 1¼ mm | 1½ mm | 1¾ mm | 2 mm | 2½ mm | 3 mm | 3½ mm | 4 mm | 5 mm |
| 49 | .41 | .78 | .14 | .51 | .88 | .64 | .41 | .19 | .99 | .63 |
| 50 | .44 | .81 | .18 | .56 | .94 | .71 | .50 | .29 | 6.11 | .77 |
| 51 | .47 | .85 | .23 | .61 | 3.00 | .78 | .58 | .39 | .22 | .92 |
| 52 | .50 | .88 | .27 | .66 | .05 | .85 | .66 | .49 | .33 | 8.06 |
| 53 | .53 | .92 | .31 | .71 | .11 | .92 | .75 | .59 | .45 | .20 |
| 54 | .55 | .95 | .35 | .76 | .17 | .99 | .83 | .69 | .56 | .34 |
| 55 | .58 | .99 | .40 | .81 | .22 | 4.06 | .92 | .79 | .67 | .48 |
| 56 | .61 | 2.02 | .44 | .86 | .28 | .13 | 5.00 | .89 | .79 | .62 |
| 57 | .64 | .06 | .48 | .91 | .34 | .21 | .09 | .99 | .90 | .76 |
| 58 | .67 | .09 | .52 | .96 | .39 | .28 | .17 | 6.09 | 7.01 | .91 |
| 59 | .70 | .13 | .56 | 3.01 | .45 | .35 | .26 | .18 | .12 | 9.05 |
| 60 | .72 | .16 | .61 | .05 | .51 | .42 | .34 | .28 | .24 | .19 |
| 61 | .75 | .20 | .65 | .10 | .56 | .49 | .43 | .38 | .35 | .33 |
| 62 | .78 | .23 | .69 | .15 | .62 | .56 | .52 | .48 | .46 | .47 |
| 63 | .81 | .27 | .73 | .20 | .68 | .63 | .60 | .58 | .58 | .61 |
| 64 | .84 | .31 | .78 | .25 | .72 | .70 | .68 | .68 | .69 | .75 |
| 65 | .87 | .34 | .82 | .30 | .79 | .77 | .77 | .78 | .80 | .90 |
| 66 | .89 | .38 | .86 | .35 | .85 | .84 | .85 | .88 | .92 | 10.04 |
| 67 | .92 | .41 | .90 | .40 | .90 | .91 | .94 | .98 | 8.03 | .18 |
| 68 | .95 | .45 | .95 | .45 | .96 | .98 | 6.02 | 7.08 | .14 | .32 |
| 69 | .98 | .48 | .99 | .50 | 4.01 | 5.05 | .11 | .17 | .26 | .46 |
| 70 | 2.01 | .52 | 3.03 | .55 | .07 | .12 | .19 | .27 | .37 | .60 |
| 71 | .04 | .55 | .07 | .60 | .13 | .19 | .28 | .37 | .48 | .74 |
| 72 | .06 | .59 | .12 | .65 | .18 | .27 | .36 | .47 | .59 | .89 |
| 73 | .09 | .62 | .16 | .70 | .24 | .34 | .45 | .57 | .71 | 11.03 |
| 74 | .12 | .66 | .20 | .75 | .30 | .41 | .53 | .67 | .82 | .17 |
| 75 | .15 | .69 | .24 | .80 | .35 | .48 | .62 | .77 | .93 | .31 |
| 76 | .18 | .73 | .29 | .85 | .41 | .55 | .70 | .87 | 9.05 | .45 |
| 77 | .21 | .76 | .33 | .90 | .47 | .62 | .78 | .97 | .16 | .59 |
| 78 | .23 | .80 | .37 | .95 | .52 | .69 | .87 | 8.06 | .27 | .73 |
| 79 | .26 | .84 | .41 | 4.00 | .58 | .76 | .95 | .16 | .39 | .87 |
| 80 | .29 | .87 | .46 | .04 | .64 | .83 | 7.04 | .26 | .50 | 12.02 |
| 81 | .32 | .91 | .50 | .09 | .69 | .90 | .12 | .36 | .61 | .16 |
| 82 | .35 | .94 | .54 | .14 | .74 | .97 | .21 | .46 | .73 | .30 |
| 83 | .38 | .98 | .58 | .19 | .81 | 6.04 | .29 | .56 | .84 | .44 |
| 84 | .40 | 3.01 | .63 | .24 | .86 | .11 | .38 | .66 | .95 | .58 |
| 85 | .43 | .05 | .67 | .29 | .92 | .18 | .46 | .76 | 10.07 | .73 |
| 86 | .46 | .08 | .71 | .34 | .98 | .26 | .55 | .86 | .18 | .86 |
| 87 | .49 | .12 | .75 | .39 | 5.03 | .33 | .63 | .96 | .29 | 13.01 |
| 88 | .52 | .15 | .80 | .44 | .09 | .40 | .72 | 9.05 | .40 | .15 |
| 89 | .55 | .19 | .84 | .49 | .15 | .47 | .80 | .15 | .52 | .29 |
| 90 | .57 | .22 | .88 | .54 | .20 | .54 | .89 | .25 | .63 | .43 |
| 91 | .60 | .26 | .92 | .59 | .26 | .61 | .97 | .35 | .74 | .57 |
| 92 | .63 | .29 | .96 | .64 | .31 | .68 | 8.06 | .45 | .86 | .71 |
| 93 | .65 | .33 | 4.01 | .69 | .37 | .75 | .14 | .55 | .97 | .85 |
| 94 | .68 | .37 | .05 | .74 | .43 | .82 | .23 | .65 | 11.08 | 14.00 |
| 95 | .71 | .40 | .09 | .79 | .48 | .89 | .31 | .75 | .20 | .14 |
| 96 | .74 | .44 | .13 | .84 | .54 | .96 | .40 | .85 | .31 | .28 |
| 97 | .77 | .47 | .18 | .89 | .60 | 7.03 | .48 | .94 | .42 | .42 |

| Inside diameter in mm | Thickness of wall in millimeters, | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 mm | 1¼ mm | 1½ mm | 1¾ mm | 2 mm | 2½ mm | 3 mm | 3½ mm | 4 mm | 5 mm |
| 98 | .80 | .51 | .22 | .94 | .65 | .10 | .57 | **10.04** | .54 | .56 |
| 99 | .83 | .54 | .26 | .99 | .71 | .17 | .65 | .14 | .65 | .70 |
| 100 | .86 | .58 | .30 | **5.08** | .77 | .24 | .74 | .24 | .76 | .84 |
| 101 | .88 | .61 | .35 | .08 | .82 | .32 | .82 | .34 | .87 | .99 |
| 102 | .91 | .65 | .39 | .13 | .88 | .39 | .91 | .44 | .99 | **15.18** |
| 103 | .94 | .68 | .43 | .18 | .94 | .46 | .99 | .54 | **12.10** | .27 |
| 104 | .97 | .72 | .47 | .23 | .99 | .53 | **9.08** | .64 | .21 | .41 |
| 105 | **8.00** | .75 | .52 | .28 | **6.05** | .60 | .16 | .74 | .33 | .55 |
| 106 | .03 | .79 | .56 | .33 | .11 | .67 | .25 | .84 | .44 | .69 |
| 107 | .05 | .82 | .60 | .38 | .16 | .74 | .33 | .93 | .55 | .83 |
| 108 | .08 | .86 | .64 | .43 | .22 | .81 | .42 | **11.03** | .67 | .98 |
| 109 | .11 | .90 | .69 | .48 | .28 | .88 | .50 | .13 | .78 | **16.12** |
| 110 | .14 | .93 | .73 | .53 | .33 | .95 | .59 | .23 | .89 | .26 |
| 111 | .17 | .97 | .77 | .58 | .39 | **8.02** | .67 | .33 | **18.00** | .40 |
| 112 | .19 | **4.00** | .81 | .63 | .45 | .09 | .76 | .43 | .12 | .54 |
| 113 | .22 | .04 | .86 | .68 | .50 | .16 | .84 | .53 | .23 | .68 |
| 114 | .25 | .07 | .90 | .73 | .56 | .23 | .93 | .63 | .34 | .82 |
| 115 | .28 | .11 | .94 | .78 | .61 | .30 | **10.01** | .73 | .46 | .97 |
| 116 | .31 | .14 | .98 | .83 | .67 | .38 | .10 | .83 | .57 | **17.11** |
| 117 | .34 | .18 | **5.03** | .88 | .73 | .45 | .18 | .93 | .68 | .25 |
| 118 | .36 | .21 | .07 | .93 | .78 | .52 | .27 | **12.02** | .80 | .39 |
| 119 | .39 | .25 | .11 | .98 | .84 | .59 | .35 | .12 | .91 | .53 |
| 120 | .42 | .28 | .15 | **6.03** | .90 | .66 | .44 | .22 | **14.02** | .67 |
| 121 | .45 | .32 | .19 | .07 | .95 | .73 | .52 | .32 | .14 | .81 |
| 122 | .48 | .35 | .24 | .12 | **7.01** | .80 | .61 | .42 | .25 | .95 |
| 123 | .51 | .39 | .28 | .17 | .07 | .87 | .69 | .52 | .36 | **18.09** |
| 124 | .53 | .43 | .32 | .22 | .12 | .94 | .78 | .62 | .48 | .23 |
| 125 | .56 | .46 | .36 | .27 | .17 | **9.01** | .86 | .72 | .59 | .37 |
| 126 | .59 | .50 | .41 | .32 | .24 | .08 | .95 | .82 | .70 | .51 |
| 127 | .62 | .53 | .45 | .37 | .29 | .15 | **11.03** | .92 | .82 | .65 |
| 128 | .65 | .57 | .49 | .42 | .34 | .22 | .12 | **18.01** | .93 | .79 |
| 129 | .68 | .60 | .53 | .47 | .41 | .29 | .20 | .11 | **15.04** | .93 |
| 130 | .70 | .64 | .58 | .52 | .46 | .36 | .28 | .21 | .15 | **19.08** |

## TABLE VII (b).

WEIGHT OF SEAMLESS COPPER TUBES PER RUNNING METER IN KILOGRAMS. (MADE BY THE ELMORE PROCESS).

| Inside diameter in mm | Thickness of wall in millimeters. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1¾ mm | 2 mm | 2½ mm | 3 mm | 3½ mm | 4 mm | 5 mm | 6 mm | 7 mm | 8 mm |
| 131 | 6.56 | 7.52 | 9.48 | 11.37 | 13.31 | 15.27 | 19.23 | 23.25 | 27.32 | 31.45 |
| 132 | .62 | .57 | .50 | .45 | .41 | .38 | .37 | .41 | .51 | .66 |
| 133 | .66 | .63 | .58 | .54 | .53 | .53 | .55 | .62 | .74 | .90 |
| 134 | .71 | .69 | .65 | .62 | .64 | .66 | .71 | .76 | .94 | 32.12 |
| 135 | .76 | .74 | .71 | .71 | .73 | .76 | .82 | .92 | 28.15 | .35 |
| 136 | .81 | .80 | .78 | .79 | .81 | .83 | .94 | 24.08 | .31 | .57 |
| 137 | .86 | .86 | .86 | .88 | .90 | .93 | 20.05 | .21 | .46 | .80 |
| 138 | .91 | .91 | .93 | .97 | 14.00 | 16.04 | .18 | .36 | .70 | 33.05 |
| 139 | .96 | .97 | 10.00 | 12.05 | .11 | .17 | .33 | .60 | .94 | .25 |
| 140 | 7.01 | 8.03 | .07 | .13 | .20 | .29 | .59 | .77 | 29.11 | .47 |
| 141 | .06 | .08 | .14 | .21 | .29 | .40 | .70 | .93 | .29 | .69 |
| 142 | .11 | .14 | .21 | .29 | .39 | .52 | .81 | 25.09 | .48 | .93 |
| 143 | .16 | .20 | .28 | .38 | .49 | .63 | .93 | .26 | .68 | 34.15 |
| 144 | .21 | .25 | .35 | .47 | .60 | .74 | 21.06 | .45 | .89 | .38 |
| 145 | .25 | .31 | .42 | .56 | .70 | .85 | .21 | .61 | 30.09 | .61 |
| 146 | .31 | .36 | .49 | .64 | .80 | .96 | .35 | .78 | .28 | .83 |
| 147 | .35 | .42 | .57 | .73 | .90 | 17.07 | .49 | .95 | .48 | 35.06 |
| 148 | .41 | .48 | .64 | .82 | 15.00 | .19 | .64 | 26.13 | .68 | .29 |
| 149 | .45 | .53 | .70 | .90 | .09 | .30 | .77 | .29 | .88 | .51 |
| 150 | .51 | .60 | .77 | .98 | .19 | .41 | .91 | .46 | 31.08 | .73 |
| 151 | .55 | .65 | .85 | 18.06 | .29 | .53 | 22.05 | .63 | .28 | .96 |
| 152 | .61 | .70 | .92 | .14 | .38 | .64 | .19 | .80 | .47 | 36.18 |
| 153 | .65 | .76 | .99 | .22 | .48 | .75 | .33 | .97 | .66 | .41 |
| 154 | .70 | .82 | 11.06 | .31 | .58 | .87 | .47 | 27.14 | .86 | .64 |
| 155 | .75 | .87 | .13 | .39 | .68 | .98 | .61 | .31 | 32.06 | .86 |
| 156 | .80 | .93 | .20 | .48 | .78 | 18.10 | .76 | .48 | .26 | 37.09 |
| 157 | .85 | .99 | .27 | .57 | .89 | .22 | .91 | .66 | .46 | .32 |
| 158 | .90 | 9.05 | .34 | .65 | .98 | .33 | 23.05 | .82 | .66 | .55 |
| 159 | .95 | .10 | .41 | .73 | 16.08 | .44 | .19 | .99 | .86 | .88 |
| 160 | 8.00 | .15 | .48 | .82 | .18 | .55 | .33 | 28.16 | 33.06 | 38.01 |
| 161 | .05 | .22 | .56 | .91 | .28 | .66 | .47 | .33 | .25 | .23 |
| 162 | .10 | .27 | .63 | 14.00 | .38 | .77 | .61 | .50 | .45 | .45 |
| 163 | .15 | .32 | .69 | .09 | .48 | .89 | .75 | .67 | .65 | .68 |
| 164 | .20 | .39 | .76 | .17 | .58 | 19.00 | .89 | .84 | .84 | .90 |
| 165 | .24 | .44 | .84 | .25 | .68 | .11 | 24.03 | 29.01 | 34.03 | 39.12 |
| 166 | .30 | .50 | .91 | .33 | .78 | .22 | .17 | .18 | .23 | .35 |
| 167 | .34 | .55 | .98 | .42 | .88 | .34 | .32 | .35 | .43 | .58 |
| 168 | .40 | .61 | 12.05 | .50 | .97 | .45 | .46 | .51 | .63 | .80 |
| 169 | .44 | .67 | .12 | .58 | 17.07 | .56 | .60 | .68 | .83 | 40.03 |
| 170 | .50 | .72 | .19 | .67 | .17 | .67 | .74 | .85 | 35.03 | .26 |
| 171 | .54 | .78 | .26 | .76 | .27 | .79 | .88 | 30.02 | .23 | .49 |
| 172 | .60 | .84 | .33 | .84 | .37 | .90 | 25.04 | .19 | .42 | .70 |
| 173 | .64 | .89 | .40 | .92 | .47 | 20.01 | .20 | .36 | .62 | .91 |
| 174 | .69 | .95 | .47 | 15.00 | .57 | .12 | .36 | .53 | .82 | 41.12 |
| 175 | .74 | 10.01 | .55 | .09 | .67 | .24 | .53 | .71 | 36.02 | .34 |

| Inside diameter in mm | Thickness of wall in millimeters. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1¾ mm | 2 mm | 2½ mm | 3 mm | 3½ mm | 4 mm | 5 mm | 6 mm | 7 mm | 8 mm |
| 176 | .79 | .06 | .61 | .17 | .76 | .35 | .65 | .87 | .21 | .57 |
| 177 | .84 | .12 | .68 | .26 | .86 | .46 | .77 | **31.04** | .41 | .81 |
| 178 | .89 | .18 | .75 | .35 | .96 | .57 | .89 | .21 | .61 | **42.05** |
| 179 | .94 | .23 | .83 | .44 | **18.06** | .69 | **26.02** | .38 | .81 | .29 |
| 180 | .99 | .29 | .90 | .53 | .16 | .81 | .15 | .55 | **37.01** | .53 |
| 181 | **9.04** | .34 | .97 | .61 | .25 | .92 | .29 | .72 | .21 | .75 |
| 182 | .09 | .40 | **18.04** | .69 | .35 | **21.03** | .43 | .89 | .41 | .97 |
| 183 | .14 | .46 | .10 | .77 | .45 | .14 | .57 | **32.06** | .62 | **43.19** |
| 184 | .19 | .51 | .18 | .85 | .55 | .25 | .71 | .23 | .83 | .41 |
| 185 | .23 | .58 | .25 | .93 | .65 | .36 | .85 | .40 | **38.04** | .63 |
| 185 | .29 | .63 | .32 | **16.01** | .75 | .47 | .99 | .57 | .25 | .86 |
| 187 | .33 | .68 | .39 | .10 | .85 | .58 | **27.13** | .74 | .46 | **44.09** |
| 188 | .39 | .74 | .46 | .18 | .95 | .70 | .27 | .91 | .67 | .32 |
| 189 | .43 | .80 | .54 | .27 | **19.05** | .82 | .42 | **33.09** | .88 | .55 |
| 190 | .49 | .85 | .60 | .37 | .15 | .94 | .57 | .25 | **39.09** | .78 |
| 191 | .53 | .91 | .67 | .45 | .24 | **22.05** | .71 | .42 | .27 | **45.00** |
| 192 | .59 | .96 | .74 | .53 | .34 | .16 | .85 | .59 | .45 | .22 |
| 193 | .63 | **11.03** | .82 | .61 | .44 | .27 | .99 | .76 | .64 | .44 |
| 194 | .68 | .08 | .89 | .69 | .54 | .38 | **28.13** | .93 | .83 | .67 |
| 195 | .73 | .13 | .96 | .77 | .64 | .49 | .27 | **34.10** | **40.02** | .90 |
| 196 | .78 | .20 | **14.03** | .86 | .74 | .60 | .41 | .27 | .21 | **46.13** |
| 197 | .83 | .25 | .09 | .95 | .84 | .72 | .55 | .44 | .40 | .36 |
| 198 | .88 | .30 | .17 | **17.04** | .94 | .84 | .69 | .61 | .59 | .59 |
| 199 | .93 | .36 | .24 | .13 | **20.04** | .96 | .83 | .78 | .78 | .82 |
| 200 | .98 | .42 | .31 | .22 | .14 | **23.08** | .98 | .95 | .97 | **47.05** |
| 201 | **10.03** | .47 | .38 | .30 | .24 | .19 | **29.12** | **35.12** | **41.16** | .27 |
| 202 | .08 | .53 | .45 | .38 | .34 | .30 | .26 | .29 | .35 | .49 |
| 203 | .13 | .59 | .52 | .46 | .44 | .41 | .40 | .46 | .55 | .71 |
| 204 | .18 | .65 | .60 | .55 | .54 | .52 | .54 | .63 | .75 | .93 |
| 205 | .23 | .70 | .66 | .63 | .64 | .63 | .68 | .80 | .95 | **48.16** |
| 206 | .28 | .75 | .73 | .72 | .74 | .74 | .82 | .97 | **42.15** | .39 |
| 207 | .33 | .81 | .80 | .80 | .84 | .85 | .96 | **36.14** | .35 | .62 |
| 208 | .38 | .87 | .88 | .89 | .94 | .96 | **30.10** | .31 | .55 | .85 |
| 209 | .43 | .93 | .95 | .97 | **21.03** | **24.08** | .24 | .48 | .75 | **49.08** |
| 210 | .48 | .99 | **15.03** | **18.06** | .13 | .20 | .39 | .65 | .95 | .31 |
| 211 | .53 | **12.05** | .10 | .14 | .23 | .31 | .53 | .81 | **43.14** | .53 |
| 212 | .58 | .10 | .16 | .23 | .33 | .42 | .67 | .98 | .33 | .75 |
| 213 | .63 | .15 | .23 | .32 | .43 | .53 | .81 | **37.15** | .53 | .97 |
| 214 | .68 | .21 | .31 | .41 | .53 | .64 | .95 | .32 | .73 | **50.20** |
| 215 | .73 | .26 | .38 | .49 | .63 | .75 | **31.09** | .49 | .93 | .43 |
| 216 | .78 | .32 | .46 | .58 | .73 | .86 | .23 | .66 | **44.13** | .66 |
| 217 | .83 | .38 | .53 | .67 | .83 | .98 | .37 | .83 | .33 | .89 |
| 218 | .88 | .44 | .60 | .75 | .93 | **25.10** | .52 | **38.00** | .53 | **51.12** |
| 219 | .93 | .50 | .67 | .83 | **22.03** | .22 | .67 | .17 | .73 | .35 |
| 220 | .99 | .56 | .74 | .92 | .13 | .34 | .82 | .34 | .93 | .58 |
| 221 | **11.03** | .61 | .81 | **19.00** | .23 | .45 | .96 | .50 | **45.12** | .80 |
| 222 | .07 | .66 | .88 | .08 | .32 | .56 | **32.10** | .67 | .31 | **52.02** |
| 223 | .12 | .72 | .95 | .16 | .42 | .67 | .24 | .84 | .51 | .24 |
| 224 | .18 | .78 | **16.02** | .25 | .52 | .78 | .38 | **39.01** | .71 | .46 |

| Inside diameter in mm | Thickness of wall in millimeters. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1¾ mm | 2 mm | 2½ mm | 3 mm | 3½ mm | 4 mm | 5 mm | 6 mm | 7 mm | 8 mm |
| 225 | .23 | .83 | .08 | .33 | .62 | .89 | .52 | .18 | .91 | .68 |
| 226 | .28 | .89 | .15 | .42 | .72 | 26.00 | .66 | .35 | 46.11 | .91 |
| 227 | .33 | .95 | .22 | .50 | .82 | .11 | .80 | .52 | .31 | 58.14 |
| 228 | .38 | 18.01 | .29 | .59 | .92 | .22 | .94 | .69 | .51 | .37 |
| 229 | .43 | .06 | .36 | .67 | 28.01 | .34 | 38.08 | .86 | .71 | .60 |
| 230 | .48 | .12 | .43 | .76 | .11 | .46 | .22 | 40.03 | .91 | .83 |
| 240 | .97 | .69 | 17.15 | 20.61 | 24.10 | 27.59 | 34.63 | 41.78 | 48.89 | 56.58 |
| 250 | 12.46 | 14.25 | .85 | 21.46 | 25.09 | 28.72 | 36.05 | 43.43 | 50.87 | 58.34 |
| 260 | — | .81 | 18.56 | 22.31 | 26.08 | 29.85 | 37.46 | 45.13 | 52.85 | 60.60 |
| 270 | — | 15.38 | 19.27 | 23.16 | 27.07 | 30.98 | 38.87 | 46.82 | 54.83 | 62.87 |
| 280 | — | .95 | .96 | 24.00 | 28.05 | 32.11 | 40.28 | 48.52 | 56.81 | 65.12 |
| 290 | — | 16.52 | 20.68 | .85 | 29.05 | 33.25 | 41.70 | 50.21 | 58.79 | 67.38 |
| 300 | — | 17.08 | 21.39 | 25.70 | 30.04 | 34.38 | 43.11 | 51.91 | 60.76 | 69.66 |
| 310 | — | .65 | 22.10 | 26.55 | 31.03 | 35.51 | 44.53 | 53.61 | 62.74 | 71.93 |
| 320 | — | 18.21 | 22.81 | 27.40 | 32.02 | 36.64 | 45.95 | 55.31 | 64.72 | 74.19 |
| 330 | — | .77 | 23.51 | 28.25 | 33.01 | 37.77 | 47.36 | 57 00 | 66.70 | 76.45 |
| 340 | — | 19.34 | 24.22 | 29.09 | 34.00 | 38.90 | 48.77 | 58.70 | 68.68 | 78.72 |
| 350 | — | .91 | 24.92 | .94 | 34.99 | 40.04 | 50.19 | 60.39 | 70.66 | 80.98 |
| 360 | — | 20.47 | 25.63 | 30.79 | 35.98 | 41.17 | 51.60 | 62 09 | 72.64 | 83.24 |
| 370 | — | 21.03 | 26.33 | 31.64 | 36.97 | 42.30 | 53.01 | 63.79 | 74.62 | 85.50 |
| 380 | — | .60 | 27.04 | 32.49 | 37.96 | 43.43 | 54.43 | 65.48 | 76.60 | 87.76 |
| 390 | — | 22.17 | .75 | 33.34 | 38.95 | 44.56 | 55.84 | 67.18 | 78.57 | 90.03 |
| 400 | — | .73 | 28.46 | 34.18 | 39.94 | 45.69 | 57.26 | 68.88 | 80.55 | 92.29 |
| 410 | — | 23.30 | 29.16 | 35.03 | 40.93 | 46.82 | 58.67 | 70.57 | 82.53 | 94.55 |
| 420 | — | .86 | .87 | .88 | 41.91 | 47.95 | 60.08 | 72.27 | 84.51 | 96.81 |
| 430 | — | 24.43 | 30.58 | 36.73 | 42.90 | 49.08 | 61.50 | 73.97 | 86.49 | 99.07 |
| 440 | — | 25.00 | 31.29 | 37.58 | 43.89 | 50.22 | 62.91 | 75.66 | 88.47 | 101.34 |
| 450 | — | .56 | 32.00 | 38.43 | 44.88 | 51.35 | 64.32 | 77.36 | 90.45 | 103.60 |
| 460 | — | 26.13 | .70 | 39.27 | 45.87 | 52.48 | 65.74 | 79.06 | 92.43 | 105.86 |
| 470 | — | .69 | 33.40 | 40.12 | 46.86 | 53.61 | 67.14 | 80.75 | 94.41 | 108.12 |
| 480 | — | 27.26 | 34.11 | .97 | 47.85 | 54.74 | 68.57 | 82.45 | 96.39 | 110.38 |
| 490 | — | .82 | 34.82 | 41.82 | 48.84 | 55.87 | 69.98 | 84.14 | 98.37 | 112.65 |
| 500 | — | 28.39 | 35.53 | 42.67 | 49.83 | 57.00 | 71.39 | 85.84 | 100.35 | 114.91 |
| 600 | — | 34.05 | 42.60 | 51.15 | 59.73 | 68.30 | 85.54 | 102.81 | 120.14 | 137.53 |

# INDEX OF NAMES.


Acheson . . . 76
Anderson . . . 39
Andreoli . . . 78

Bauer . . . 39
Brandt . . . 69
Brown . . . 122, 129
Buchholz . . . 9
Burdette . . . 131
Burgess . . . 45

Chassy . . . 3
Cowper-Coles . . . 64, 91, 108

Davis . . . 106
Dessolle . . . 63
Dumoulin . . . 42, 125

Electro-Metallurgical Co . . . 46
Electricitäts-Aktien-G., V. Schuckert & Co . . . 52
Elektrogravure G. Ltd. Elmore . . . 45, 75, 105, 117
Elmore, German and Austro-Hungarian Co . . . 45, 47, 49, 53, 108
Elkington . . . 76
Edruweit . . . 61, 70
Engelhart . . . 38, 46, 10, 104
Evans . . . 106

Fletcher . . . 38, 91
Foerster . . . 4, 22, 23, 26
Forsyth . . . 91
Fox . . . 76

Gerhardi & Co . . . 49

Hall . . . 133
Hampe . . . 26
Hartig . . . 22
Haubold . . . 106
Hittorf . . . 8
Holborn . . . 29
Holl . . . 44
Hoepfner . . . 55
Huber . . . 60
Hübl, von . . . 6, 15, 25

Jakobi . . . 1
Jordan . . . 1

Kennedy . . . 122
Kick . . . 15
Kirchoff . . . 37
Klein . . . 93
Kohlrausch . . . 29
Krueger . . . 106